



Japanese Journal of Tribology

Volume 40, Number 12, 1995

Development of Solid Lubricants for High Temperature Rolling Ceramic Bearings (Part 1): Various Solid Lubricants Based on Fluoride Compounds

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An attempt was made to develop solid lubricants needed for the application of rolling ceramic bearings under high temperature conditions above 500°C. Solid lubricant coatings were applied to heat resistant alloy surfaces by combining calcium fluoride (CaF₂), barium fluoride (BaF₂), silver (Ag), chromium oxide (Cr₂O₃), and bismuth oxide (Bi₂O₃) and using the vacuum plasma spraying method. The friction characteristics of the resulting coatings were determined by performing high temperature reciprocating friction and wear tests, in which the friction coefficient μ was measured over a wide temperature range from room temperature to 900°C. The best friction characteristics were found in the case of CaF₂ + BaF₂ + Cr₂O₃ coatings, the friction coefficient being $\mu = 0.2-0.3$ over a wide temperature range (300 to 900°C). A small friction coefficient in this case was attributed to the simultaneous presence of CaF₂ and BaCrO₄ that was formed during an increase in temperature. In addition, the lubricating property of coatings at 800°C was evaluated by evaluation tests of retainer material simulating a

Received November 10, 1995. Due to the pressing production schedule this article is printed without any changes or corrections from the author(s). Allerton Press, Inc. is solely responsible for the accuracy of this translation.

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bearing. The friction coefficient of $\text{CaF}_2 + \text{BaF}_2 + \text{Cr}_2\text{O}_3$ coatings was found to be 0.1 and friction characteristics and the adhesive property of surfaces were excellent. Their practical realization can be expected.

1. INTRODUCTION

The heat resistance, wear resistance, and resistance to corrosion of rolling ceramic bearings are exceptionally better than bearings made from steel and their application under specific conditions can be expected. In this work, application under high temperature conditions was examined and problems related to the lubricating method and appropriate lubricants were studied.

When using solid lubricants, lubricating techniques such as the method of direct-contact surface improvement of rolling contact surfaces (the surface improvement method) [1], the method of supplying lubricant from the retainer by adhesion (adhesive method) [2,3], and the method of forced supply of a lubricant from outside the bearing (method of forced supply) [4,5] are used.

On the other hand, applications under temperature conditions above 500°C are possible only by using solid lubricants where, in general, hexagonal boron nitride is used. However, studies on other lubricants, such as Bi_2O_3 [6], Cr_2O_3 [6,7], $\text{CaF}_2 + \text{BaF}_2$ [8], $\text{CaF}_2 + \text{BaF}_2 + \text{Ag}$ [9], and $\text{Na}+2+\text{ZrO}_3 + \text{Cr}_2\text{O}_3$ [10], have been carried out. These are also used as solid lubricants for the retainer of the rolling bearing but their adhesive property and wear behavior (wear resistance) have not been practically evaluated.

In these studies, solid lubricants for rolling ceramic bearings capable of operating efficiently both under high temperature conditions and in air were developed to be applied using the adhesive method. It was expected that the application of these lubricants would prolong the lifetime of bearings without any modification of their structure. In this work, the results obtained by the formation of a coating of these solid lubricants and the evaluation of their lubricating properties (friction characteristics, wear behaviors, and adhesive properties) are presented. These results indicate that lubricating properties of developed lubricants are much better than those of any high-temperature solid lubricants that have been used until now.

These studies were carried out as a joint effort of the Institute of Technology and the Society of Mechanics (Company) as "Studies on Advanced Surface Modification Technology."

2. THE METHOD OF APPLYING SOLID LUBRICANT COATING AND THE METHOD OF EVALUATION

2.1. Solid lubricant application method

Five kinds of powders were chosen as solid lubricants. These were calcium fluoride (CaF_2), barium fluoride (BaF_2), silver (Ag), chromium oxide (Cr_2O_3), and bismuth oxide (Bi_2O_3). Then, since it was impossible to form a solid lubricant coating (referred to as a coating below) by using only a solid lubricant powder, a powder of heat-resistant Ni alloy (Ni-23.2 Co-17.0 Cr-12.5 Al-0.5 Y) was used as a binder. Flat test specimens were prepared from Ni-Cr alloy (Inconel® 713 C), the dimensions of test specimens being $70\text{ mm} \times 17\text{ mm} \times 14\text{ mm}$.

The powder used for the coating was prepared as follows. First, solid lubricant powders were mixed in the proportions shown in Table 1. Then, the binder was added in an amount to make its

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2.2. Method

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Table 1

Mixture ratio of solid lubricant during application of solid lubricant coatings.

Symbol of solid lubricant coating	Mixture ratio of solid lubricant, mass %
CB	40 CaF ₂ +60 BaF ₂
CBA	20 CaF ₂ +30 BaF ₂ +50 Ag
CBCr	20 CaF ₂ +30 BaF ₂ +50 Cr ₂ O ₃
Cr	100 Cr ₂ O ₃
BCr	50 BaF ₂ +50 Cr ₂ O ₃
Bi	100 Bi ₂ O ₃
CBCrA	CBCrA/3 13 CaF ₂ +20 BaF ₂ +33 Cr ₂ O ₃ +33 Ag
	CBCrA/4 15 CaF ₂ +23 BaF ₂ +38 Cr ₂ O ₃ +25 Ag
CBCrBi	13 CaF ₂ +20 BaF ₂ +34 Cr ₂ O ₃ +33 Bi ₂ O ₃

Table 2

Vacuum plasma spraying conditions.

Process	Plasma gas, MPa		Current, A	Environmental pressure, kPa	Carrier gas, MPa
	Ar	He			
Sputter cleaning 1	0.69 (100)	—	600	2.66	—
Preliminary heating		0.69 (100)	700		
Sputter cleaning 2		—	800		
Spraying	0.34 (50)	1.03 (150)	800	6.65	0.20 (30)

Note: Inside () value in psi units.

Distance between spraying gun and test specimen: 250 mm. Plasma discharge voltage: DC 40 V constantly.

proportion 80 vol %. (Since the volume proportion of the binder strongly influences the powder supply during the formation of the coating by spraying, the adherence of the coating to the flat test specimen, and the coating strength, it was added to a constant vol %. However since the powder supply was rather poor in the case of applying Cr coatings, the level of the volumetric content of the binder was raised to 90 vol %). Conditions for which the formation of coatings from these powders are accomplished are given in Table 2. In this case, coatings of 0.4-1.0 mm in thickness were formed on flat test specimens of 70 mm by 17 mm by using the vacuum plasma spraying method. In the discussion below, the coating symbols shown in Table 1 are used for identification.

2.2. Method of solid lubricant coating evaluation

To evaluate friction properties of coatings, high-temperature reciprocating friction and wear tests and retainer material evaluation tests were performed.

Table 3
Conditions of high-temperature reciprocating friction and wear test.

Item	Conditions
Load	9.8N
Reciprocation speed	7.5 reciprocation/min
Speed of sliding	1.75mm/s (Average)
Temperature	Room temperature \rightarrow 100°C \rightarrow 900°C (or 1000°C) \rightarrow 100°C \rightarrow room temperature (interval 100°C)
Counterpart material	Sphere of silicon nitride 5/16"

To evaluate friction characteristics over a wide temperature range, the high-temperature reciprocating friction and wear testing machine [11] shown in Fig. 1 was used. Test conditions are given in Table 3. Surfaces with coatings were machined by grinding to a coating thickness of 0.3-0.4 mm and together with counterpart spheres of silicon nitride they were degreased and cleaned before testing. The friction coefficient μ was measured during a temperature rise and a temperature drop, each temperature level being maintained for 5 min for measurements.

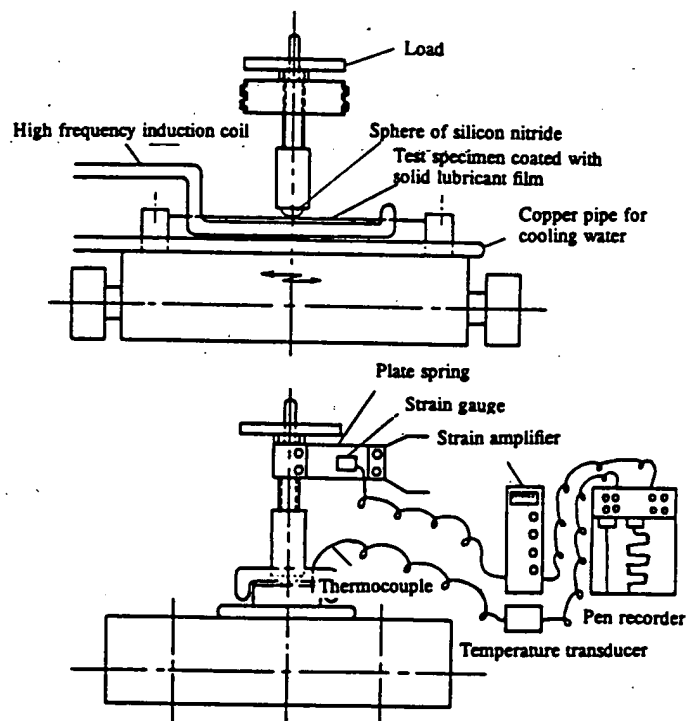
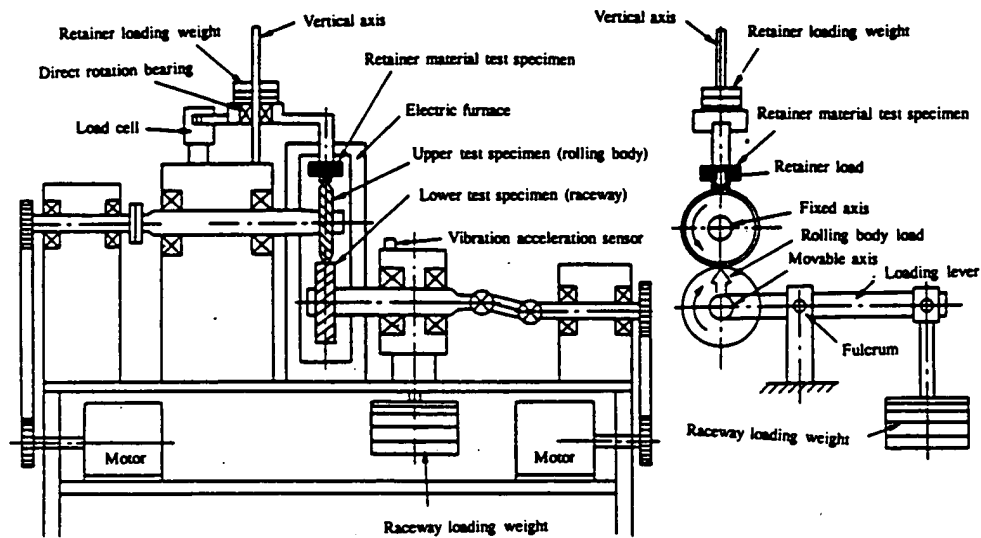
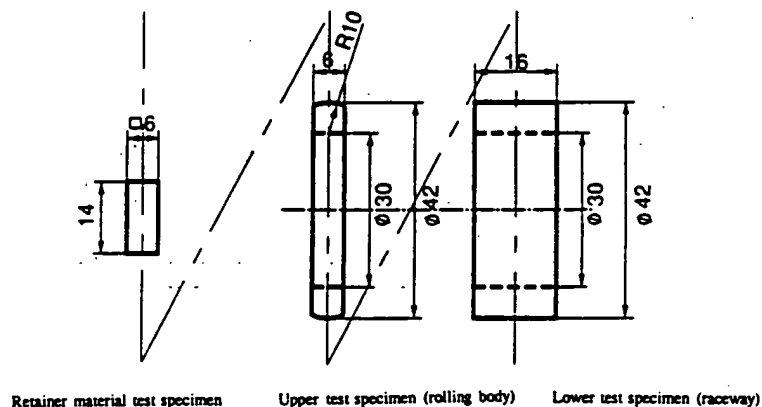


Fig. 1
Schematic diagram of high-temperature reciprocating friction and wear testing machine.

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(a) Schematic diagram of tester



(b) Shapes of test specimens

Fig. 2
Schematic diagram of tester for evaluation of retainer material.

When evaluating lubricating properties (friction characteristics, wear behaviors, and adhesive properties) of coatings at a constant temperature, a tester allowing evaluation of the simulated retainer material [12] at the contact state of a rolling bearing, as shown in Fig. 2 (sliding contact between retainer and rolling body and rolling contact between rolling body and raceway) was used. Tests were run as follows: after the running-in of the retainer material test specimen against the lower test specimen, corresponding to a rolling body for 10 min, the upper test specimen and the lower test specimen corresponding to the raceway were brought into contact and tested. Test conditions are given in Table 4. During the tests, the friction between the retainer material test specimen and the upper test specimen was measured for evaluation of friction characteristics of coatings. Also, the vibration acceleration at the axis of rotation of the lower test specimen was observed in order to evaluate the state of adhesion.

Table 4
Conditions for evaluation testing of retainer material.

Item	Conditions
Material of upper and lower test specimens	Silicon nitride
Number of revolutions of upper and lower test specimens	1000 rpm
Speed of sliding of retainer material test specimen and upper test specimen	2.2 m/s
Load { Retainer load	20 N
Bearing load	200 N
Temperature	800°C
Environmental atmosphere	Atmosphere

3. RESULTS OBTAINED BY HIGH-TEMPERATURE RECIPROCATING TESTING FOR FRICTION AND WEAR

3.1. Friction characteristics of solid lubricant coatings

Friction characteristics of CB coatings were evaluated with the purpose verifying the studies of Sliney [8]. The results obtained are shown in Fig. 3. It is evident from the figure that the friction coefficient is large in a wide temperature range (from room temperature to 900°C). Therefore, the authors made an attempt to reduce the friction coefficient by adding other solid lubricants to the CB coating base and by changing component proportions.

When comparing results obtained on CBA coatings consisting of a CB coating into which Ag was added with those obtained on CB coatings, a slight reduction of the friction coefficient was found in the temperature range below 500°C and an increase of the friction coefficient was observed in the

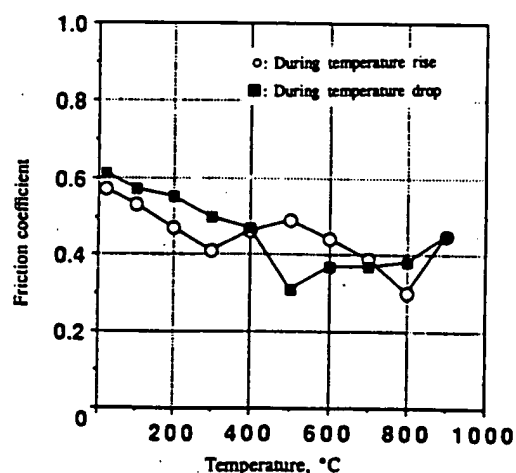


Fig. 3
Friction characteristics of CB solid lubricant coating.

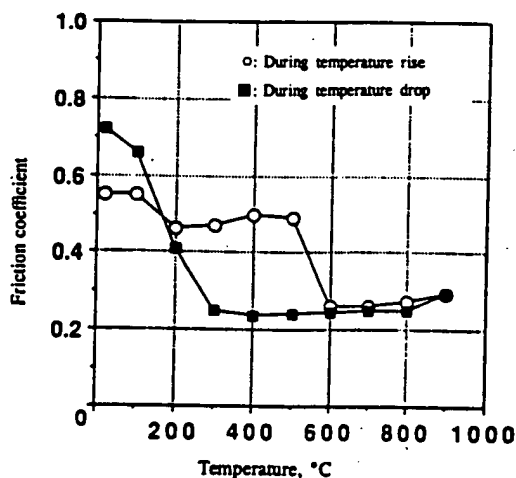


Fig. 4
Friction characteristics of CBCr solid lubricant coating.

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temperature region above 700°C. The friction coefficient in this case was higher than that of the CBA coating of Sliney [9], which it could have been formed under different conditions. The reason for an increase of the friction coefficient in the high temperature region in the present case of CB coating was attributed to the oxidation of Ag.

Then an attempt was made to add Cr₂O₃ to CB. Prior adding tests on Cr coatings containing Cr₂O₃ only (binder content 90 vol%) were performed. It was found that $\mu = 0.3-0.5$ and friction characteristics were as good as those reported until now [6,7]. In the case of CBCr coatings in which Cr₂O₃ was added, a reduction of the friction coefficient was observed during a temperature rise to above 500°C; during a temperature drop from 900°C, the friction coefficient was as low as less than 0.3 and was stable (see Fig. 4). An improvement of friction characteristics of CB coating was particularly noticeable in the temperature region beyond 600°C.

With the purpose of improving the friction characteristics of CBCr coatings in the temperature region under 300°C (temperature rise to above 500°C), Ag was added to CBCr coatings, thus forming a CBCrA coating. Friction characteristics were determined in the case of the CBCrA/3 coating, the Ag content of which was 1/3 of the total weight of the solid lubricant components, and also in the case of CBCrA/4, in which it amounted to 1/4. The results showed a decrease of the friction coefficient in the temperature range below 300°C with the addition of Ag and an increase of the friction coefficient in the temperature region above 600°C. This tendency grew more noticeable with an increasing Ag content. The effect of the addition of Ag was similar to that when Ag was added to the CB coating and it was found that these combinations could not be utilized as solid lubricants in the temperature region of above 500°C, which was the target temperature range in these studies.

It has been reported [6] that Bi₂O₃ showed good friction characteristics under high temperature conditions. To verify these results, tests on Bi coatings containing Bi₂O₃ alone were performed. The results showed that in the temperature range below 500°C, the friction coefficient was comparatively large and it grew small in the temperature region of above 700°C. In particular, at 1000°C, the friction coefficient was $\mu = 0.18$. Therefore, an attempt to add Bi₂O₃ was made to reduce the friction coefficient of CBCr coating in the high temperature region. However, the friction coefficient of CBCrBi coating was rather large within the entire temperature region and it showed irreproducible and unstable behavior. It was established that the addition of Bi₂O₃ had no effect.

However, results obtained by evaluating friction characteristics using this test method are distinguished by a large friction coefficient in the low temperature range and a low friction coefficient in the high temperature range during a temperature rise and a temperature drop (see Figs. 3 and 4). The reason for this behavior is the fact that when approaching the melting point, solid lubricants soften, which results in a reduction of the friction coefficient.

3.2. Reproducibility of friction characteristics in CBCr coatings

To verify the reproducibility of the friction behavior of CBCr coatings that showed most favorable friction characteristics, tests were performed by using a high-temperature reciprocating friction and wear testing machine. Friction tests during a temperature rise and during a temperature drop will be called the temperature cycle. The temperature cycle that was performed until the formation of friction traces on two different sites of one test specimen was repeated twice in succession on another similar test specimen until the formation of similar friction traces. Also, in this case, the friction coefficient decreased when temperature rose above 500°C and decreased when temperature dropped below 400°C. Also, in each case, the friction coefficient was small and stable at each level. It follows from the above results that CBCr coatings are stable and offer good reproducibility.

3.3. Lubricating mechanisms of the coatings under consideration

In the case of CBCr coatings, different phenomena that appear in the friction coefficient behavior during a temperature rise and a temperature drop in the temperature range 200-600°C (called hysteresis phenomena below) are more conspicuous than in other solid lubricant coatings. These phenomena are thought to be related to mechanisms of lubrication by CBCr coatings. Therefore, at each temperature level (room temperature → 400°C → 500°C → 600°C → 700°C → 900°C → 400°C → room temperature), X-ray diffraction analysis was performed on test specimens with CBCr coatings that had been tested on the high-temperature reciprocating friction and wear testing machine only once. BaF₂ and Cr₂O₃, the formation of which during the coating formation was verified, were not observed at each temperature level but the formation of a new compound of barium chromate (BaCrO₄) was established. Typical diffraction patterns and test results are shown in Fig. 5. It was also established that the crystalline state of BaCrO₄ was that of the rhombic crystal system. Graphite and molybdenum disulfide are known as typical solid lubricants that are laminated compounds having cleavage planes. Most compounds of this kind are hexagonal crystal systems of rhombic crystal structure [13]. Consequently, it can be suggested that BaCrO₄ is a laminated compound with cleavage planes.

It was supposed that the presence of BaCrO₄ contributed to better friction characteristics even in the absence of CaF₂; therefore, the evaluation of the friction behavior of BCr coating was done by performing high-temperature reciprocating tests for friction and wear. However, X-ray diffraction analysis showed that the friction coefficient was as small as anticipated in a range of $\mu = 0.3-0.7$, irrespective of whether BaCrO₄ was observed in coatings after testing for friction and wear or not. It was also found that the presence of BaCrO₄ did not always mean good friction characteristics; however CaF₂ played an important role. In the case of the CaF₂ + BaF₂ type solid lubricant of Sliney, who was a pioneer in this field, studies were repeatedly performed by considering CaF₂ as a compound with cleavage planes [14]. These facts and the test results obtained in these studies allow the conclusion that CBCr coatings show excellent friction characteristics because of the presence of CaF₂ and BaCrO₄, which have cleavage planes.

However, despite the formation of BaCrO₄, hysteresis, phenomena appearing during the second thermal cycle were similar to those appearing in the first thermal cycle. This is explained as follows.

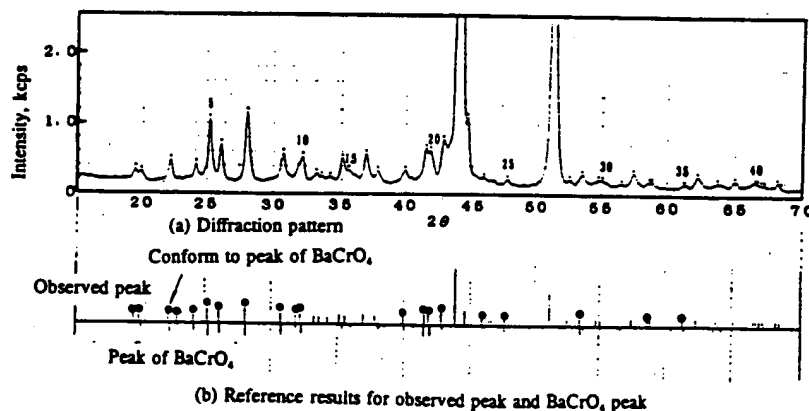


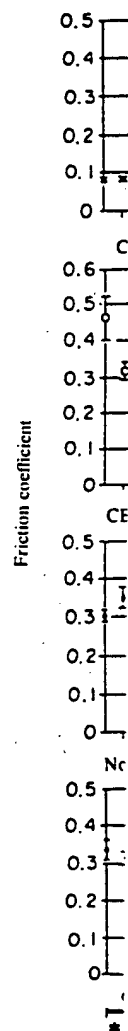
Fig. 5

Results obtained by X-ray diffraction analysis of CBCr solid lubricant coating that confirm formation of BaCrO₄.

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At temperatures above 600°C, BaCrO₄ is formed from BaF₂ and Cr₂O₃ by supplying oxygen from the atmosphere. BaCrO₄ formed in this way, together with CaF₂, promotes good friction characteristics during a temperature drop to about 300°C, but at temperatures below 300°C, the friction coefficient increases and wear proceeds due to a reduction of BaCrO₄ formed on the sliding surface through wear. Therefore, hysteresis phenomena appearing during the second thermal cycle are similar to those appearing during the first thermal cycle.

3.4. Results obtained by retainer material evaluating tests

Evaluation of the lubricating property by using the retainer material evaluation tester was accomplished on four test specimens: a test specimen with CBCr coating that had shown the best

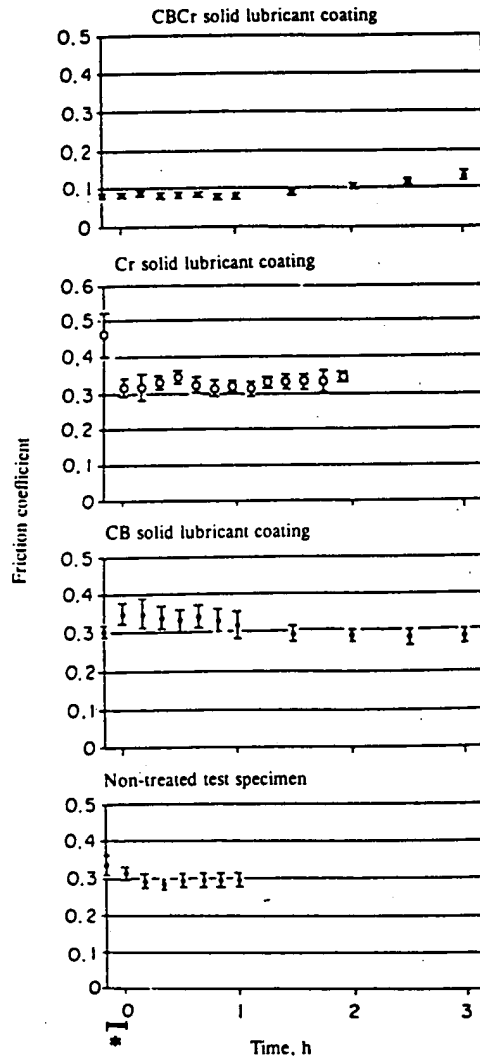


Fig. 6
Successive records of friction coefficient.
*Running-in

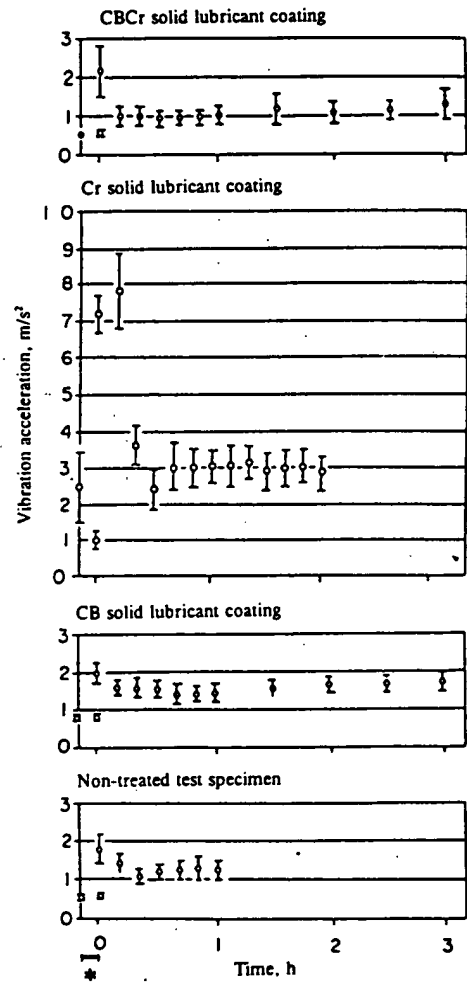


Fig. 7
Successive records of vibration.
*Running-in

friction characteristics in high-temperature reciprocating friction and wear tests on different coatings, a test specimen with CB coating, a test specimen with Cr coating, and a non-treated flat test specimen, the latter three latter specimens being used for the sake of comparison. Tests were performed for 1-3 hours using the procedure described above. In the process of testing, the friction coefficient and the vibration acceleration were recorded. The results are shown in Figs. 6 and 7.

The friction coefficient for CBCr coating is likely to reduce somewhat with time and become as small as 0.1. In the cases when Cr coating and CB coating were used, the friction coefficient was larger than that for non-treated test specimen, which was 0.3 or comparable. The friction coefficient of less than that of about 0.25 observed at 800°C during the high-temperature reciprocating test for

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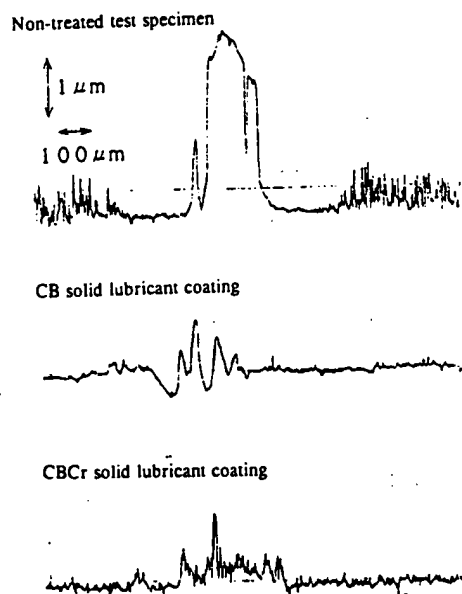


Fig. 8

Form of friction traces in axial direction on lower test specimens.

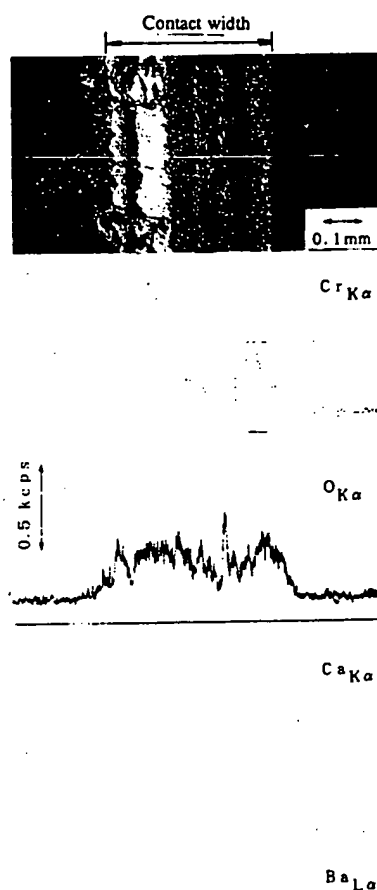


Fig. 9

Adhesion state of CBCr solid lubricant at friction traces on lower test specimen.

friction and wear was explained by a higher speed of sliding; 70 Cr₃C₂ + 15 Ag + 15 CaF₂/BaF₂ (mass%) type solid lubricant developed by Sliney from NASA [9] showed the speed of sliding to be 2.7 m/s and the friction coefficient to be about 800°C, amounting to $\mu = 0.3$; however the CBCr coating formed in these studies showed higher friction characteristics.

On the other hand, the vibration on CBCr coating was minimal compared to that of the non-treated test specimen; the vibration on CB and Cr was larger than that on the former test specimens. Considering the amplitude of variation of the friction coefficient to be smaller than that of the non-treated test specimen, it was suggested that CBCr coating evenly adhered to the lower test specimen through the upper test specimen made from silicon nitride.

To verify this adhesion ability, the adhesion state of the lower test specimen was observed. The results obtained by measurements of the shape in the axial direction of the lower test specimen are shown in Fig. 8. When the lower test specimen was used in combination with the non-treated test specimen, an intensive adhesion was found in the region adjacent to the center of the contact zone. In the case of contact with CB coating, the adhesion was insignificant and traces of irregular adhesion and wear were observed. On the other hand, when sliding against CBCr coating, the formation of a thin uniform adhesion layer was clearly observed. In the case of combining with CB coating, wear on the lower test specimen amounted to about 0.5 μm but when sliding against other test specimens only the presence of the adhesion layer was found and no wear was observed.

Figure 9 shows the results obtained by examination using EPMA linear analysis of the state of adhesion in the contact zone of the lower test specimen, which was different from that used for testing CBCr coating shown in Fig. 8. As is evident from the figure, in the region in which the adhesion is observed, the almost uniform distribution of elements Cr, O, Ca, and Ba, which compose the structure of the solid lubricant, is found. This means that the formation of the adhesion layer proceeds rather effectively.

The wear resistant property, which is one of the lubricating characteristics, was estimated from the wear rate on the coatings. When sliding against the CBCr coating, the wear rate on the region with wear traces on the non-treated test specimen was 30 μm in each case. However, since the test time for the non-treated test specimen did not exceed 1/3 of that for CBCr coating, it was concluded that the wear resistance of CBCr coating was much better.

When comparing the cross-sectional structure of CBCr coating with that of the non-treated test specimen, the porosity was observed (see Fig. 10). Irrespective of the high wear resistance, this

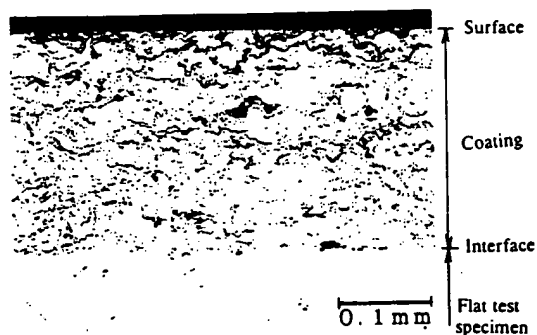


Fig. 10
Cross-sectional structure of CBCr solid lubricant coating
(photograph by optical microscopy).

porosity in combination with the friction property and the adhesion property, promotes the maintenance of good lubrication conditions.

It follows from the above results that excellent lubricating properties of CBCr coating are provided by the superposition of the friction property, the adhesion property, and the wear resistance.

4. CONCLUSION

The lubrication method and lubricants used for rolling ceramic bearings under temperature conditions exceeding 500°C present serious problems for study. In this work, assuming the application of the adhesive lubrication method, powders of calcium fluoride (CaF_2), barium fluoride (BaF_2), silver (Ag), chromium oxide (Cr_2O_3), and bismuth oxide (Bi_2O_3) were used in combination to form solid lubricant coatings by the vacuum plasma spraying method and friction characteristics of resulted coatings were determined. The following results were obtained in these studies.

(1) When evaluating by the high-temperature reciprocating friction and wear test method, $\text{CaF}_2 + \text{BaF}_2 + \text{Cr}_2\text{O}_3$ coatings showed excellent friction characteristics, the friction coefficient being $\mu = 0.2-0.3$ in a wide temperature range (from 300 to 900°C).

(2) When testing $\text{CaF}_2 + \text{BaF}_2 + \text{Cr}_2\text{O}_3$ coatings by the retainer material evaluation method with the speed of sliding being 2.2 m/s and at 800°C, a friction coefficient of $\mu = 0.1$ was established. Also, the observation and analysis of the surface of test specimens showed the formation of a thin uniform adhesive layer, which indicated at good adhesive property of the coatings under consideration. Wear on test specimens was not observed and the wear rate of coatings was rather low.

(3) Friction characteristics of $\text{CaF}_2 + \text{BaF}_2$ coatings were improved when Ag and Bi_2O_3 were added.

It follows from the above that $\text{CaF}_2 + \text{BaF}_2 + \text{Cr}_2\text{O}_3$ solid lubricant coatings offer excellent lubricating properties and their application to high-temperature self-lubricating retainers of rolling ceramic bearings can be expected.

Finally, the authors express their gratitude to Mr. Kazunori Umeda, the head of the research group of the Institute of Technology, Mr. Hirobuni Kojimai, the head of the research group, Mr. Hiroshi Kashimura from the NTN Co., Mr. Makoto Takamori from the Kawasaki Heavy Industries Co., Mr. Eiji Hirai from the Nippon Bakkara Itching Co. and Mr. Hiromi Sugi from the Nippon Seiko Co. for their assistance during the performance of these studies.

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Japanese Journal of Tribology

Volume 41, Number 2, 1996

Development of Solid Lubricant for High Temperature Ceramic Rolling Bearings (Part 2): Ternary System Solid Lubricants Composed of $\text{CaF}_2 + \text{BaF}_2$ and Cr_2O_3

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In the former report the lubrication characteristics of a $\text{CaF}_2 + \text{BaF}_2 + \text{Cr}_2\text{O}_3$ system solid lubricant in a high temperature atmosphere in air were reported. In this report an evaluation of this solid lubricant was carried out concerning the lubrication characteristics when the percentages of the mix of the solid lubricant and binder, as well as, the percentages of the mix of the constituents of the solid lubricant ($\text{CaF}_2 + \text{BaF}_2$ and Cr_2O_3) were changed. As a result it became clear that the most superior lubrication characteristics were shown when the percentages of the mix of the constituents of the solid lubricant $\text{CaF}_2 + \text{BaF}_2$ and Cr_2O_3 are 50:50 (mass %). Further, from the result of high temperature X-ray diffraction, that BaCrO_4 is formed in the coat of solid lubricant and that excellent friction characteristics are shown in the temperature range from 700°C to 1,000°C, due to coexistence with CaF_2 , was confirmed, following the previous report.

Received November 10, 1994.

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1. INTRODUCTION

In the previous report [1] the lubrication characteristics (friction, abrasion, and transfer characteristics) of various solid lubricant coatings, formed by the reduced pressure plasma flame coating method (with the objective of putting ceramic rolling bearings to practical use in a high temperature atmosphere that exceeds 500°C in air), were evaluated, studied, and reported.

The authors have attempted to develop a better solid lubricant by changing the composition percentages of the solid lubricant components and the mix percentages of the solid lubricant and binder, with reference to the $\text{CaF}_2 + \text{BaF}_2 + \text{Cr}_2\text{O}_3$ system solid lubricant coating that showed excellent lubricant characteristics in the previous report.

This essay discusses trial manufactured solid lubricant coatings; the results of an evaluation of the friction characteristics, abrasion characteristics, and transfer characteristics by means of cage material testing and an evaluation machine that imitates the contact status of rolling bearings are related. The results are also reported on an evaluation of the friction characteristics in the high temperature range, from room temperature up to 900°C, by means of a high temperature reciprocating friction abrasion testing machine.

2. EXPERIMENTAL METHOD

2.1. Solid lubricant coating formation method

Table 1 shows the composition of the solid lubricant coatings that were submitted for testing. Powders of three types, CaF_2 , BaF_2 , and Cr_2O_3 , were used as solid lubricants. The basic material of the test pieces that formed the solid lubricant coating were made of Ni-Cr alloy (Inconel[®] 713 C), as in the previous report, and the shape of the test pieces was 70 L × 17 W × 14 H (mm). Furthermore, since the solid lubricant by itself will not adhere to the test piece, an Ni group alloy (Ni-23.2 Co-17.0 Cr-12.5 Al-0.5Y) powder was used as a binder. The formation of the solid lubricant coating was carried out by the same method as in the previous report.

2.2. Observation, analysis, and the cage material evaluation test

The friction characteristics, abrasion characteristics, and transfer characteristics, when the solid lubricant coating was applied to the rolling bearings, were evaluated under test conditions used by the cage material evaluation and testing machine of the previous report, as shown in Table 2.

In order to clarify the causes of differences in the friction, abrasion, and transfer characteristics of the solid lubricant coatings that were subjected to the cage material evaluation test, the rolling contact portion of the lower part of the test piece was observed and analyzed by means of a scanning electron microscope (SEM) and an X-ray microanalyzer (EPMA) after the cage material evaluation test.

2.3. High temperature reciprocating friction abrasion test and analysis

The friction characteristics in the wide temperature range (room temperature-900°C) of the solid lubricant coatings were evaluated using the high temperature reciprocating friction abrasion testing machine of the previous report.

The test was conducted under the same conditions as in the previous report. Measurement of the coefficient of friction was carried out at each temperature (100°C intervals), when the temperature was rising and falling, after the coefficient of friction had stabilized.

Table 1
Composition of solid lubricant coating.

Test piece No.	Blend ratio of the components of the solid lubricant, mass % $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3$	Mix ratio of the solid lubricant and the binder, vol % Solid lubricant : binder
1	50:50	10:90
2	50:50	20:80
3	50:50	30:70
4	50:50	40:60
5	40:60	20:80
6	60:40	20:80

Binder: Ni-23.2 Co-17.0 Cr-12.5 Al-0.5Y

Table 2
Cage material evaluation test conditions.

Classification	Content
Rotating speed	1000 rpm (sliding speed of the rolling elements and the cage material test piece = 2.2 m/s)
Set temperature	800°C temperature of the atmosphere inside the furnace
Load	Cage material test piece - rolling element: 4.9 N Rolling element - bearing ring: 200 N
Atmosphere	Air

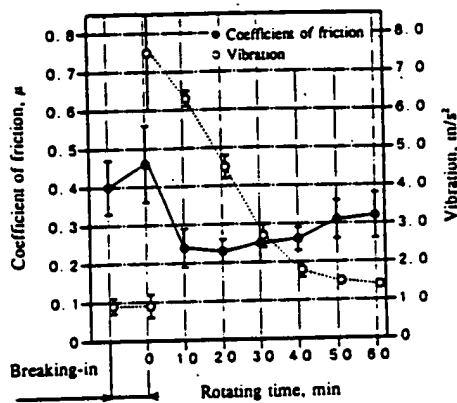
For the solid lubricant coatings that showed good lubrication characteristics over a wide range of temperatures, the existence configuration of the solid lubricants in the coatings was confirmed by means of high temperature X-ray diffraction.

3. EXPERIMENTAL RESULTS AND CONSIDERATIONS

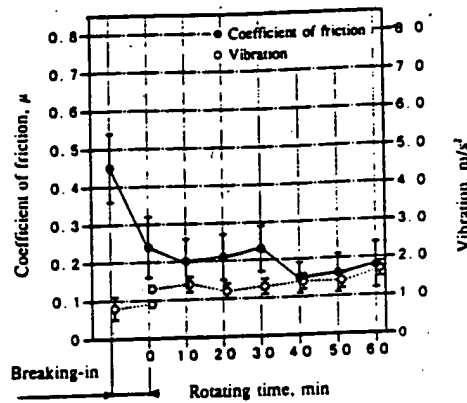
3.1. Cage material evaluation test results

Figure 1 shows the changes with the passage of time of the vibrations and Table 1 shows the coefficients of friction of the lubricant coatings. Figure 1 and Table 1 show (1) the case of the blend ratio of the solid lubricant components ($\text{CaF}_2 + \text{BaF}_2$, Cr_2O_3) fixed at 50:50 (mass %) with a solid lubricant coating (test pieces No. 1, 2, 3, and 4) in which the mix ratio of solid lubricant and binder is changed, and (2) the case of the mix ratio of the solid lubricant and the binder fixed at 20:80 (vol %) with a solid lubricant coating (test pieces No. 2, 5, and 6) in which the blend ratio of the solid lubricant components changes.

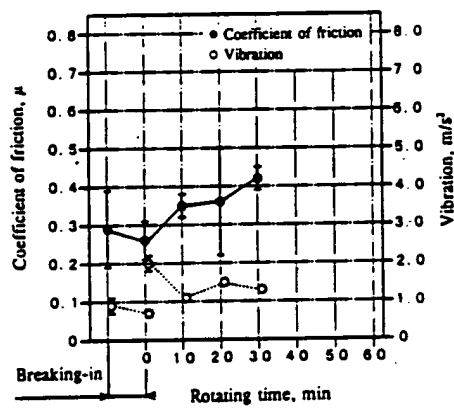
Concerning (1), in test piece No. 2 of Fig. 1(b), the coefficient of friction decreased during the breaking-in and, from the start of the actual test, became stable over time at a value of about 0.2. Vibration became stable over time at a value of about 1.5 m/s^2 from the start of the actual test.



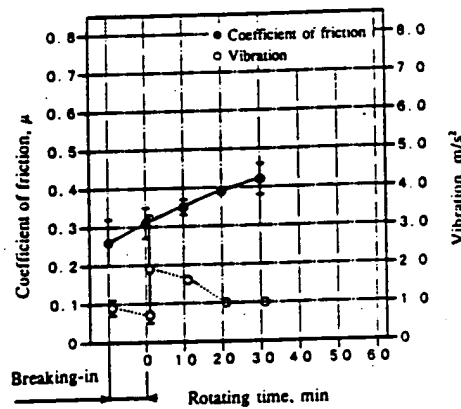
(a) Test piece No. 1
Solid lubricant:binder=10:90 (vol%)
 $\text{CaF}_2 + \text{BaF}_2:\text{Cr}_2\text{O}_3 = 50:50$ (mass %)



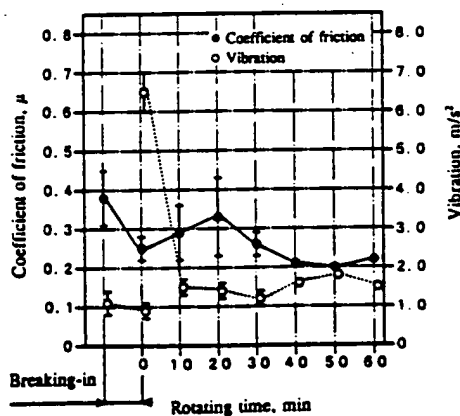
(b) Test piece No. 2
Solid lubricant:binder=20:80 (vol%)
 $\text{Ca} + \text{BaF}_2:\text{Cr}_2\text{O}_3 = 50:50$ (mass %)



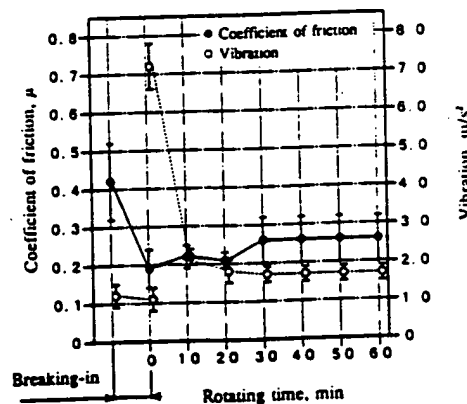
(c) Test piece No. 3
Solid lubricant:binder=30:70 (vol%)
 $\text{CaF}_2 + \text{BaF}_2:\text{Cr}_2\text{O}_3 = 50:50$ (mass %)



(d) Test piece No. 4
Solid lubricant:binder=40:60 (vol%)
 $\text{CaF}_2 + \text{BaF}_2:\text{Cr}_2\text{O}_3 = 50:50$ (mass %)



(e) Test piece No. 5
Solid lubricant:binder=20:80 (vol%)
 $\text{CaF}_2 + \text{BaF}_2:\text{Cr}_2\text{O}_3 = 40:60$ (mass %)



(f) Test piece No. 6
Solid lubricant:binder=20:80 (vol%)
 $\text{CaF}_2 + \text{BaF}_2:\text{Cr}_2\text{O}_3 = 60:40$ (mass %)

Fig. 1
Cage material evaluation test result.

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In contrast to this, in test piece No. 1 of Fig. 1(a), the coefficient of friction did not decrease at during the breaking-in, decreased after the start of the actual test to about 0.25, and showed a tendency to increase steadily after that. Vibration immediately after the start of the actual test increased to 7.5 m/s^2 , but subsequently it steadily decreased and stabilized at a value of about 1.5 m/s^2 .

As for test piece No. 3 of Fig. 1(c), the coefficient of friction decreased at the time of breaking-in, but after the start of the actual test steadily increased and stabilized at a high value of about 0.35. Vibration became high after the start of the actual test, but immediately decreased and stabilized at a value of about 1 m/s^2 .

As for test piece No. 4 of Fig. 1(d), the coefficient of friction continued to gradually increase from the time of breaking-in and stabilized at a high value of about 0.42 after the start of the actual test. Vibration became high after the start of the actual test but immediately decreased and stabilized at a value of about 1 m/s^2 . Furthermore, concerning test pieces No. 3 and 4, at the point when the coefficient of friction exceeded 0.4, the test aborted.

From the above, for (1), it became clear that the solid lubricant coating of test piece No. 2 showed superior lubrication characteristics.

Next, concerning (2), for test piece No. 5 of Fig. 1(e), the coefficient of friction decreased at the time of breaking-in, but did not stabilize, became high again after the start of the actual test, and finally stabilized at a value of about 0.2. Vibration after the start of the actual test increased to 6.5 m/s^2 , but immediately decreased and stabilized at a value of about 1.5 m/s^2 .

For test piece No. 6 of Fig. 1(f), the coefficient of friction decreased at the time of breaking-in, but after the start of the actual test gradually increased and stabilized at about 0.25. Vibration after the start of the actual test increased to 7.2 m/s^2 , but immediately decreased and stabilized at about 1.8 m/s^2 .

Also from the above, for (2), it became clear that the solid lubricant coating of test piece No. 2 showed superior lubrication characteristics.

From this it became clear, for the mix ratio of solid lubricant and binder, that in the case of a mix ratio of 20:80 (vol %) both the coefficient of friction and the vibration stabilized at low levels, and for the blend ratio of the solid lubricant components, both the coefficient of friction and vibration stabilized at low levels in the case of a blend ratio of 50:50 (mass %).

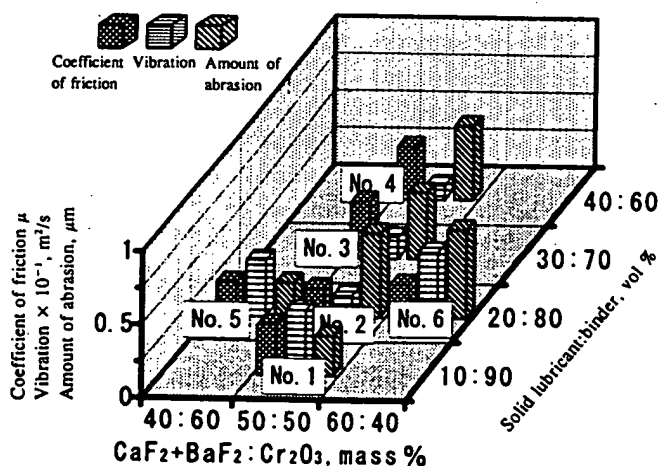


Fig. 2
Compilation of cage material evaluation test results.

3.2. Cage material evaluation test result considerations

Figure 2 shows a compilation of the results of the measurements of the wear of the rolling contact parts of the lower parts of the test pieces that correspond to the respective solid lubricant coatings and the average values of the coefficients of friction and vibration of the solid lubricant coatings shown in Table 1. The amount of abrasion is the depth of the abrasion of the central part of the rolling contact part. Furthermore, the abrasion wear of test pieces No. 3 and 4 of Fig. 2 is the value of a 30 minute

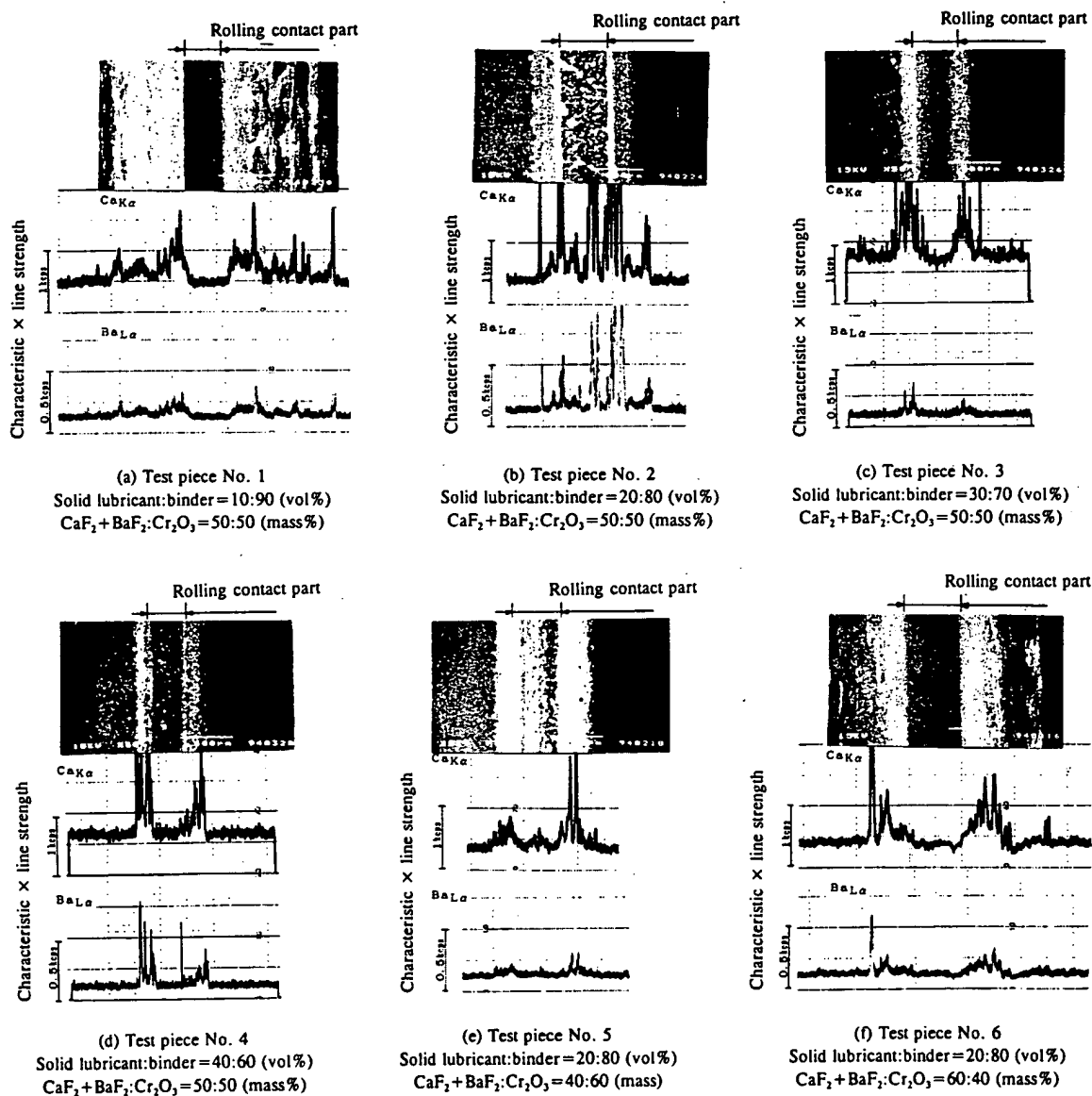


Fig. 3

Results of component analysis by means of EPMA and SEM observation results.

test. The abrasion wear of the other test pieces are for 60 minute tests. Figure 3 shows the results of analysis by means of the SEM images and EPMA of the rolling contact parts of the lower part of the test pieces that correspond to the solid lubricant coatings of Table 1.

According to Fig. 2, it can be seen that the coefficient of friction and vibration that occurs in the rolling contact portion of the upper part of the test piece and the lower portion of the test piece show the best results when the blend ratio of the solid lubricant components is 50:50 (mass %) and the mix ratio of the solid lubricant and the binder is 20:80 (vol %).

The possible reason for this, according to Fig. 3, is that in the lower part of the test pieces that correspond to the respective solid lubricant coatings, a transfer film was perceived on the rolling contact part of the lower part of the test pieces that corresponded to test pieces No. 2 and No. 5 with a 20:80 (vol %) mix ratio of lubricant and binder, and that much solid lubricant existed in the transfer film of test piece No. 2 with a 50:50 (mass %) blend ratio of solid lubricant components and, moreover, that it was evenly distributed.

Next, the amount of abrasion is considered from Figs. 2 and 3. When it is considered that the test times of test pieces No. 3 and 4 were 30 minutes, in the case in which the mix ratio of solid lubricant and binder was changed, a tendency for the amount of abrasion to increase was perceived following an increase in the percentage of solid lubricant in the mix. Furthermore, in the case in which the blend ratio of the solid lubricant components was changed, a tendency was perceived towards a reduction of the abrasion amount and for transfer film to be left on the rolling contact part following an increase in the percentage of Cr_2O_3 in the blend.

The possible reason for this is that following an increase in the percentage of solid lubricant in the mix inside the coating, the coating becomes brittle and easily abraded, and even if there is transfer, in a short time the lubrication film is consumed and the amount of abrasion of the lower part of the test piece becomes larger. On the other hand, for the blend ratio of solid lubricant components, it was thought that since the coating becomes easy to transfer following an increase of Cr_2O_3 in the solid lubricant components, and the residue of transfer film on the rolling contact part of the lower part of the test piece becomes greater with the increase of Cr_2O_3 , the amount of abrasion decreased due to the lubrication of the transfer film. Furthermore, on the upper part of the test pieces that corresponds to all of the test pieces, a transfer film exists and abrasion was not perceived.

3.3. High temperature reciprocating friction abrasion test results and considerations

Figure 4 shows the changes of the coefficient of friction with respect to the temperature of the respective solid lubricant coatings. They are shown (1) in the case of lubricant coatings (test pieces No. 1, 2, 3, and 4) that fix the blend ratio of the solid lubricant components at 50:50 (mass %) and change the mix ratio of the lubricant and binder, and (2) in the case of lubricant coatings (test pieces No. 2, 5, and 6) that fix the mix ratio of the lubricant and binder at 20:80 (vol %) and change the blend ratio of the lubricant components. Figure 5 shows the consolidated results of measurements of the amounts of wear after the tests of the respective solid lubricant coatings. The amount of abrasion is indicated by the average value of the abrasion depth of the center and both ends of the abrasion mark.

From Fig. 4, for (1), in test pieces No. 2, 3, and 4 of Fig. 4(b),(c),(d), the coefficient of friction decreased in the temperature range of 700°C to 800°C when the temperature was rising and from 800°C to 400°C when the temperature was falling, but in test piece No. 1 of Fig. 4(a), the coefficient of friction did not decrease when the temperature was rising or falling. A possible reason for this is that in the coatings of test pieces No. 2, 3, and 4 there was a sufficient amount of the necessary solid lubricant, but in the coating of test piece No. 1 the amount of solid lubricant was too little.

Concerning (2), in test pieces No. 5 and 6 of Fig. 4 (e),(f), the coefficient of friction decreased only in the temperature range of 700°C to 500°C when the temperature was falling.

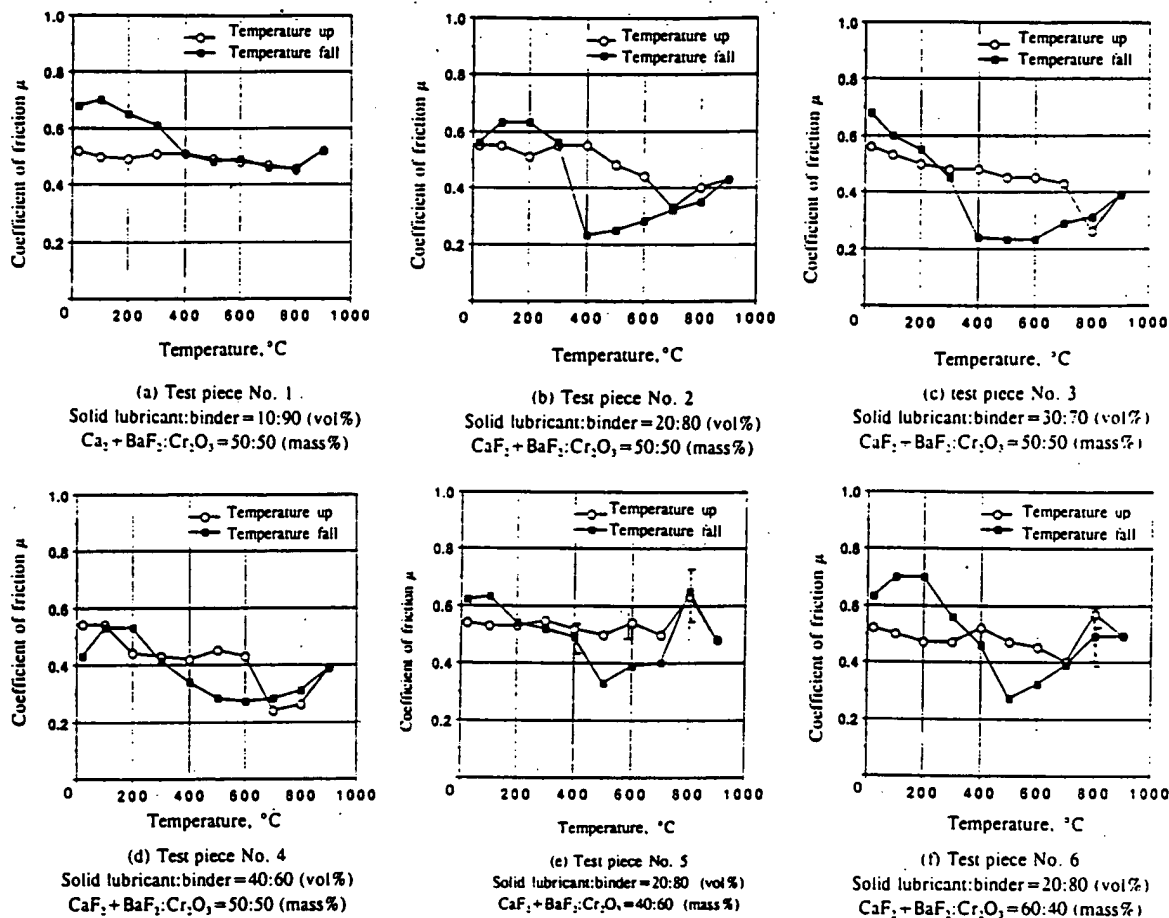


Fig. 4
Results of high temperature reciprocating friction abrasion tests.

From the above results it became clear that in the case of a mix percentage of 20 vol % or more of solid lubricant, solid lubricant exists in the coating, and a decrease in the coefficient of friction with respect to the temperature can be perceived; furthermore, in the case of a blend ratio of 50:50 (mass %) of solid lubricant components, the temperature range that decreases the coefficient of friction is the widest.

From Fig. 5 it became clear that the amount of abrasion of the coating increased after increases in the percentage of solid lubricant in the solid lubricant coating mix, and furthermore, after increases in the percentage of the blend of Cr_2O_3 in the components of the solid lubricant.

Next, in order to clarify the relationship between the temperature range that decreases the coefficient of friction and the temperature that forms the substance (BaCrO_4) that can be regarded as conducive to lubrication in the coating (for the solid lubricant coating that was not submitted to the high temperature reciprocating friction abrasion test formed at the same time as test piece No. 2), the existing configuration of the solid lubricant in the coating with respect to temperature was analyzed by means of high temperature X-ray diffraction from room temperature to 970°C at 100° intervals. In Fig. 6, the analysis results at 700°C or more (970°C) are shown.

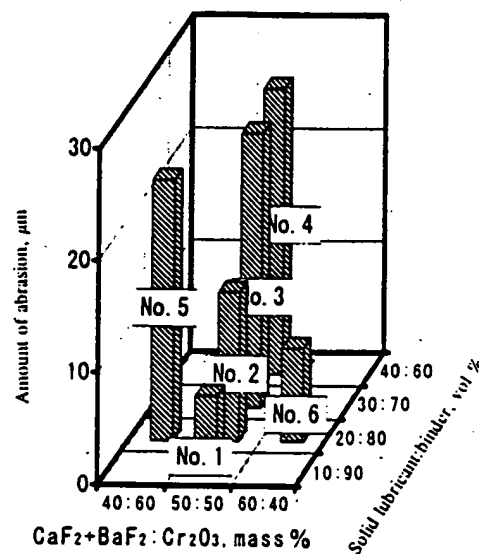
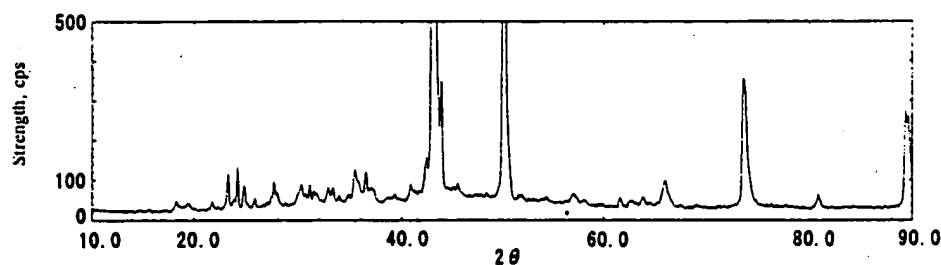
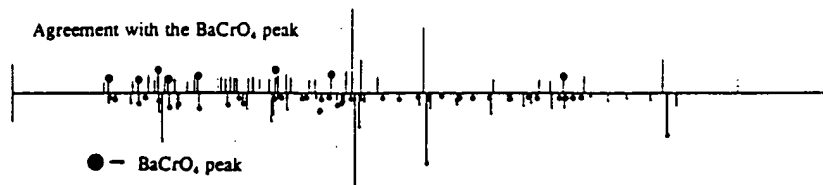


Fig. 5

Amount of abrasion of the solid lubricant coating after the high temperature reciprocating friction abrasion test.



(a) Diffraction pattern



(b) Collated result of the observed peak and the BaCrO₄ peak

Fig. 6

High temperature X-ray diffraction results that confirm the formation of BaCrO₄ at 700°C and above.

From the results of the analysis it is clear that from room temperature to 600°C no particular change was perceived in the existing configuration of the solid lubricant in the coating, but at 700°C and above, BaCrO₄, which had not existed in the coating until then, was formed. Thus it became clear that a correlation exists between the formation of BaCrO₄ in the coating and the test results that showed that the coefficient of friction decreases from 700°C when the temperature is rising and to 400°C when the temperature is falling, and, as mentioned in the previous report, due to the coexistence with CaF₂, excellent friction characteristics are shown. Furthermore, the reason the coefficient of friction increased at 300°C and below has been mentioned in the previous report.

4. CONCLUSION

In solid lubricant coatings formed by means of the reduced pressure plasma flame coating method, for the cases in which the mix ratio of the solid lubricant and the binder and the blend ratio of the solid lubricant components changed, the following became clear as a result of evaluating their friction characteristics, abrasion characteristics, and transfer characteristics.

(1) In the results of the cage material evaluation tests, it was seen that a solid lubricant coating with a 50:50 (mass %) blend ratio of solid lubricant components and a 20:80 (vol %) mix ratio of solid lubricant and binder showed best friction characteristics, abrasion characteristics, and transfer characteristics as a solid lubricant for ceramic rolling bearing use.

(2) As a result of observations with a scanning electron microscope and analysis by means of an X-ray microanalyzer, for the case of a solid lubricant coating with a 20:80 (vol %) mix ratio of solid lubricant and binder and a 50:50 (mass %) blend ratio of solid lubricant components, it became clear that the amount of solid lubricant existing in the transfer film of the rolling contact part of the lower part of the test pieces increased, and also the solid lubricant was uniformly distributed.

(3) In the high temperature reciprocating friction abrasion tests, it was seen that in solid lubricant coatings with a blend percentage of solid lubricants of 20 vol % or more, the coefficient of friction decreased over a wide temperature range and also in the case in which a blend ratio of solid lubricant components was 50:50 (mass %), the coefficient of friction showed the lowest, stable value; furthermore, the coating became easier to abrade following increases in the percentage of solid lubricant in the solid lubricant coating blend and in the percentage of Cr₂O₃ in the solid lubricant component mix.

(4) The results of high temperature X-ray diffraction made clear that at a temperature of 700°C or above, BaCrO₄ is formed in the solid lubricant coating, that a correlation exists between the lowering of the coefficient of friction and the formation of BaCrO₄ in the coating, and that excellent friction characteristics are shown due to coexistence with CaF₂.

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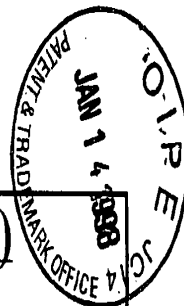
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Table 1 Comparison of NASA and Japanese Coatings



<u>Coating</u>	<u>Binder (vol %)</u>	<u>Hardener (vol %)</u>	<u>Lubricants (vol %)</u>
Claimed Invention ^a	NiCr (50)	Cr ₂ O ₃ (27)	Ag(6)+BaF ₂ /CaF ₂ (17) ^c
CBCrA ^b	NiCoCrAlY(80%)	Cr ₂ O ₃ (7%)	Ag(3)+BaF ₂ (6)+CaF ₂ (4)

a - For example, original specification Table 2

b - Toyota Part 1, p. 1279, Table 1

c - Prefused fluoride eutectic

Table 2 Useful Operating Temperature Range

<u>Coating</u>	<u>Lower Limit</u>	<u>Upper Limit</u>	<u>Comments</u>
Claimed Invention ^d	-200°C	850°C	No degradation following repeated thermal cycles
CBCrA ^e	25°C	600°C	Thermal cycling above 500°C causes irreversible chemical reactions degrading tribological performance (high friction and wear below 300°C)

d - For example, original specification Table 3

e - Toyota Part 1, p. 1283, para. 3 and p. 1285, para. 1

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DEVELOPMENT OF HIGH-TEMPERATURE SOLID LUBRICANTS
FOR ROLLING CERAMIC BEARING (Part II)
-Ternary System Solid Lubricant Composed of $\text{CaF}_2 + \text{BaF}_2$ and Cr_2O_3 -
[Seramikku Korogari Jikuuke yo Koon Kotai Junkatsuzai no
Kaihatsu (Dainiho)]

Hiroshi Toyota, Takeo Yoshioka, Kazunori Umeda
Shin Niizeki, Toshiaki Kaneko and Takashi Itakura

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Translated Title : Development of High-Temperature Solid Lubricants for Rolling Ceramic Bearing (Part II)
-Ternary System Solid Lubricant Composed of CaF₂+BaF₂ and Cr₂O₃-

Foreign Title : Seramikku Korogari Jikuuuke yo Koon Kotai Junkatsuzai no Kaihatsu (Dainiho)

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Source : トライボロジスト (**Tribologists**), 41
(2), 146-153 (1996) (Japanese)

¹Numbers in the margin indicate pagination in the foreign text.

I. INTRODUCTION

Aiming at the practical use of rolling ceramic bearing in a high-temperature atmosphere of above 500°C, we reported results of evaluations and studies on the lubricating properties (frictional property, wear property and transfer property) of various solid lubricant films formed by reduced pressure plasma spray method in a previous paper¹.

The authors attempted to develop a more excellent solid lubricant by changing the mixing ratio of solid lubricant to binder and the compounding ratio of solid lubricant components of a $\text{CaF}_2 + \text{BaF}_2 + \text{Cr}_2\text{O}_3$ solid lubricant films which exhibited excellent lubricating properties in the previous paper.

In this paper, we will describe results of evaluating the frictional property, wear property and transfer property of trial solid lubricant films by a cage material evaluation testing machine which simulates the contact state of rolling bearing. We will also report results of evaluating the frictional property in a tempera-
ture range from room temperature to 900°C by a high-temperature reciprocating friction wear testing machine. /147

II. EXPERIMENTAL METHODS

2.1 Method for forming solid lubricant films

The composition of solid lubricant films supplied for tests is shown in Table 1. Three kinds of powder of CaF_2 , BaF_2 and Cr_2O_3

were used as the solid lubricant. A parent material of specimens for forming the solid lubricant films was similarly made from a Ni-Cr alloy (Inconel® 713C) as in the previous paper, and the shape of specimens was taken as 70Lx17Wx14H (mm). Moreover, a Ni-base alloy (Ni-23.2, Co-17.0, Cr-12.5, Al-0.5Y) powder was used as the binder only in the solid lubricant because it does not adhere to the specimens.

The solid lubricant films were formed by the same method as in the previous paper.

Table 1
Composition of Solid Lubricant Films

Specimen No.	Compounding Ratio of Solid Lubricant Components mass% $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3$	Mixing Ratio of Solid Lubricant to Binder vol% Solid Lubricant : Binder
1	50 : 50	10 : 90
2	50 : 50	20 : 80
3	50 : 50	30 : 70
4	50 : 50	40 : 60
5	40 : 60	20 : 80
6	60 : 40	20 : 80

Binder : Ni-23 Co-17 Cr-12.5 Al-0.5 Y

2.2 Cage material evaluation tests, observation and analysis

The frictional property, wear property and transfer property of solid lubricant films in their application to rolling bearing were evaluated under test conditions shown in Table 2 by a cage

material evaluation testing machine in the previous paper.

To clarify reasons for differences in frictional property, wear property and transfer property of solid lubricant films provided for the cage material evaluation tests, the rolling contact part of lower specimens after the cage material evaluation tests was observed and analyzed by scanning electron microscope (SEM) and X-ray microanalyzer (EPMA).

Table 2
Conditions for Cage Material Evaluation Tests

Item	Content
Rotational speed	1,000 rpm (sliding velocity of cage material specimen and rolling element = 2.2m/s)
Set temperature	800°C temperature of atmosphere in oven
Load	cage material specimen-rolling element : 4.9 N rolling element-track roller : 200 N
Atmosphere	Atmospheric air

2.3 High-temperature reciprocating friction wear tests and analysis

The frictional property of solid lubricating films in a wide temperature range (room temperature-900°C) was evaluated by a high-temperature reciprocating friction wear testing machine in the previous paper.

The tests were made under the same conditions as in the previous paper, and the friction coefficient was measured at

temperatures (100°C interval) during raising or lowering temperature after the friction coefficient was stabilized.

The existence form of solid lubricant films exhibiting a good lubricating properties in a wide temperature range was confirmed by high-temperature X-ray diffraction.

3. EXPERIMENTAL RESULTS AND EXAMINATION

3.1 Results of cage material evaluation tests

Fig. 1 is time-elapsd changes of friction coefficient and vibration of solid lubricant films shown in Table 1. They show (1) cases of solid lubricant films (specimen Nos. 1, 2, 3, 4) whose compounding ratio of solid lubricant components ($\text{CaF}_2 + \text{BaF}_2$, Cr_2O_3) to binder is taken as constant at 50:50 (mass%) and mixing ratio of solid lubricant to binder is changed, and (2) cases of solid lubricant films (specimen Nos. 2, 5, 6) whose mixing ratio of solid lubricant ($\text{CaF}_2 + \text{BaF}_2$, Cr_2O_3) to binder is taken as constant at 20:80 (vol%) and mixing ratio of solid lubricant to binder is changed.

In regard to (1), with specimen No. 2 of Fig. 1(b), the friction coefficient decreased in the run-in operation and then stabilized with time at a value of ca. 0.2 from the beginning of this test. The vibration stabilized with time at a value of ca. 1.5 m/s^2 from the beginning of this test.

With specimen No. 1 of Fig. 1(a), by contrast, the friction coefficient did not decrease in the run-in operation, decreased after the beginning of this test and became a value of ca. 0.25,

then tended to increase slowly. The vibration increased to 7.5 m/s² immediately after the beginning of this test, then slowly decreased and stabilized at a value of ca. 1.5 m/s².

With specimen No. 3 of Fig. 1(c), the friction coefficient

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decreased in the run-in operation, slowly increased after the beginning of this test and stabilized at a high value of ca. 0.35. The vibration increased after the beginning of this test, but decreased right away and then stabilized at a value of ca. 1 m/s².

With specimen No. 4 of Fig. 1(d), the friction coefficient continued to increase slowly from the run-in operation, and stabilized at a high value of ca. 0.42 after the beginning of this test. The vibration increased after the beginning of this test, but decreased right away and then stabilized at a value of ca. 1 m/s². Moreover, the test was discontinued at the point when the friction coefficients of specimens No. 3 and No. 4 were more than 0.4.

From the above, it became clear that the solid lubricant film of specimen No. 2 exhibited the most excellent lubricating property.

Next, in regard to (2), with specimen No. 5 of Fig. 1(e), the friction coefficient decreased in the run-in operation but did not stabilize, then increased again after the beginning of this test, and finally stabilized at a value of ca. 0.2. The vibration increased to 6.5 m/s², but decreased right away and

stabilized at a value of ca. 1.5 m/s^2 .

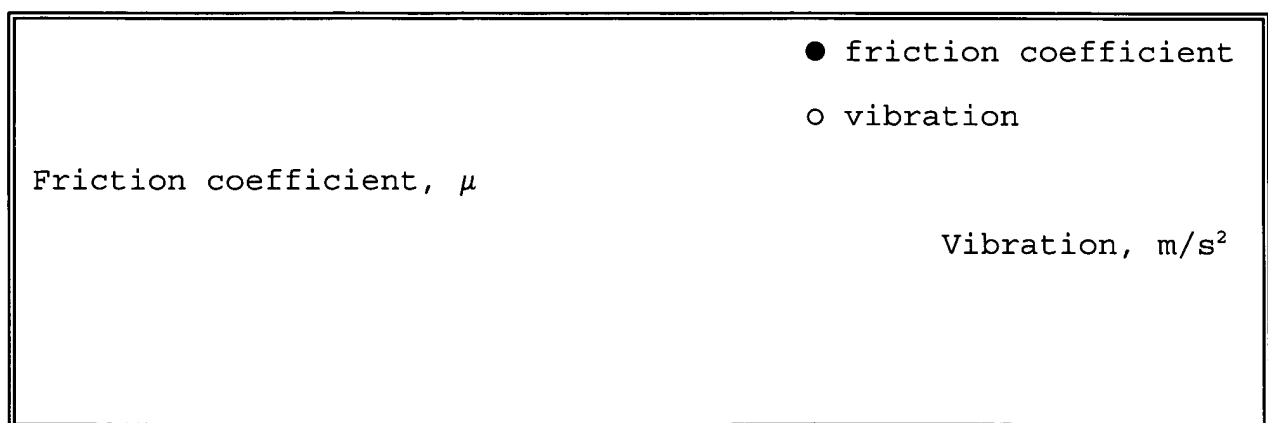
With specimen No. 6 of Fig. 1(f), the friction coefficient decreased in the run-in operation, but slowly increased after the beginning of this test and stabilized at a value of ca. 0.25. The vibration increased to 7.2 m/s^2 , but decreased right away and stabilized at ca. 1.8 m/s^2 .

From the above, it was clarified that the solid lubricant film of specimen No. 2 in (2) also exhibited the most excellent lubricating property.

Accordingly, it became clear that both the friction coefficient and vibration were low and stabilized when the mixing ratio of solid lubricant to binder was made to 20:80 (vol%), and both the friction coefficient and vibration were low and stabilized when the compounding ratio of solid lubricant components was made to 50:50 (mass%).

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Figs. 1 Results of Cage Material Evaluation Tests



run-in
operation

Rotational time, min

● friction coefficient
○ vibration

Friction coefficient, μ

Vibration, m/s^2

Rotational time, min

● friction coefficient
○ vibration

Friction coefficient, μ

Vibration, m/s^2

Rotational time, min

(c) Specimen No. 3
solid lubricant : binder = 30:70 (vol%)
 $\text{CaF}_2 + \text{BaF}_2$: Cr_2O_3 = 50:50 (mass%)

	● friction coefficient
	○ vibration
Friction coefficient, μ	
	Vibration, m/s^2

run-in
operation

Rotational time, min

(d) Specimen No. 4
solid lubricant : binder = 40:60 (vol%)
 $\text{CaF}_2 + \text{BaF}_2$: Cr_2O_3 = 50:50 (mass%)

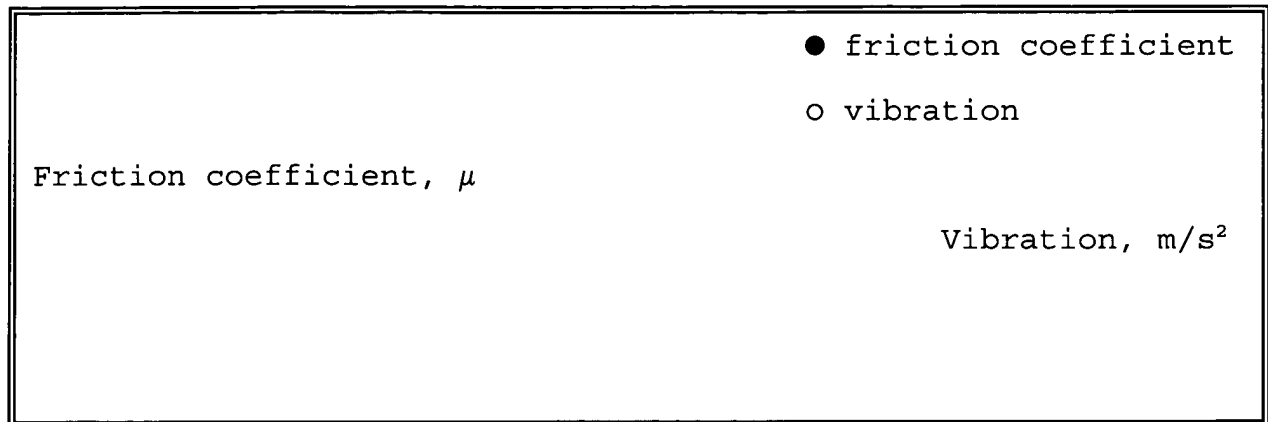
	● friction coefficient
	○ vibration
Friction coefficient, μ	
	Vibration, m/s^2

run-in
operation

Rotational time, min

(e) Specimen No. 5
solid lubricant : binder = 20:80 (vol%)

$\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 40:60$ (mass%)



run-in
operation

Rotational time, min

(f) Specimen No. 6
solid lubricant : binder = 20:80 (vol%)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 60:40$ (mass%)

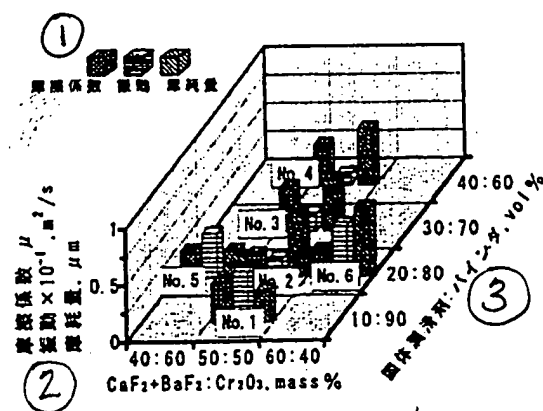
/149 (cont'd.)

3.2 Examination on results of cage material evaluation tests

The average values of the friction coefficient and vibration of solid lubricant films shown in Table 1 and measuring results of abrasion loss in the rolling contact part of lower specimens corresponding to respective solid lubricant films are summarized and shown in Fig. 2. The abrasion loss is the wearing depth in the center of rolling contact part. Moreover, the abrasion loss of specimens No. 3 and No. 4 of Fig. 2 is values at the testing time of 30 min, and the abrasion loss of other specimens is values at the testing time of 60 min. Fig. 3 is analytical

results based on SEM images and EPMA of rolling contact part of lower specimens corresponding to solid lubricant films of Table 1.

Fig. 2 Summary of cage material evaluation test results



- (1) friction coefficient vibration abrasion loss
- (2) friction coefficient, μ
- (3) solid lubricant : binder, vol%

From Fig. 2, it is known that the friction coefficient of solid lubricant films and the vibration generated in the rolling contact part of upper specimen and lower specimen gives the best results when the mixing ratio of solid lubricant to binder is 20:80 (vol%) and the compounding ratio of solid lubricant components is 50:50 (mass%).

As a reason for it, it is considered from Fig. 3 that a transfer film is found in the rolling contact part of lower specimens corresponding to specimens No. 2 and No. 5 whose mixing ratio of solid lubricant to binder is 20:80 (vol%), and that considerable solid lubricant exists and uniformly distributes in the transfer film of specimen No. 2 whose compounding ratio of

solid lubricant components is 50:50 (mass%).

Next, the abrasion loss is examined from Fig. 2 and Fig. 3. If it is considered that the testing time of specimens No. 3 and No. 4 is 30 min, such a tendency that the abrasion increases with increasing the mixing ratio of solid lubricants is found in the case of changing the mixing ratio of solid lubricant to binder. Moreover, such tendencies that the abrasion decreases with increasing the compounding ratio of Cr_2O_3 and a transfer film remains in the rolling contact part are found in the case of changing the compounding ratio of solid lubricant components.

As a reason for it, it was considered that the films became brittle and was easy to wear with increasing the mixing ratio of solid lubricant in the films, the lubricating film was attrited in a short time even if it transferred, thus the abrasion of lower specimens increased. On the other hand, it was considered that the transfer film became easy to transfer with the increase of Cr_2O_3 in the solid lubricant components with regard to the compounding ratio of solid lubricant components, therefore the remainder of transfer film in the rolling contact part of lower specimens increased, and the abrasion loss due to the lubrication of transfer film decreased. Moreover, the transfer film existed in the upper specimens corresponding to all specimens, thus the abrasion was not found.

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Figs. 3 SEM observation results and component analytical results

rolling contact part

Property x line intensity

(a) specimen No. 1

solid lubricant : binder = 10:90 (vol%)

$\text{CaF}_2 + \text{BaF}_2$: Cr_2O_3 = 50:50 (mass%)

rolling contact part

Property x line intensity

(b) specimen No. 2

solid lubricant : binder = 20:80 (vol%)

$\text{CaF}_2 + \text{BaF}_2$: Cr_2O_3 = 50:50 (mass%)

rolling contact part

Property x line intensity

(c) specimen No. 3

solid lubricant : binder = 30:70 (vol%)

$\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 50:50$ (mass%)

rolling contact part

Property x line intensity

(d) specimen No. 4

solid lubricant : binder = 40:60 (vol%)

$\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 50:50$ (mass%)

rolling contact part

Property x line intensity

(e) specimen No. 5

solid lubricant : binder = 20:80 (vol%)

$\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 40:60$ (mass%)

rolling contact part

Property x line intensity

(f) specimen No. 6

solid lubricant : binder = 20:80 (vol%)

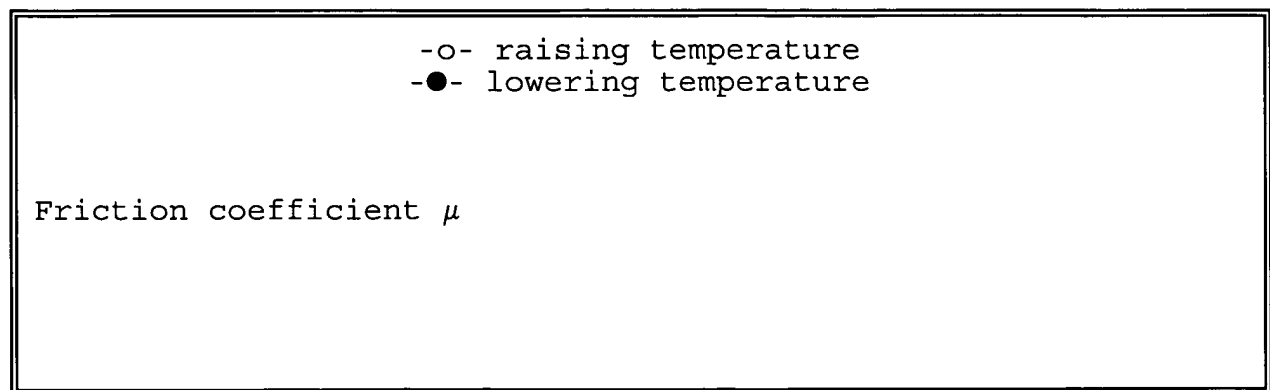
$\text{CaF}_2 + \text{BaF}_2$: Cr_2O_3 = 60:40 (mass%)

3.3 Results of High-temperature reciprocating friction wear tests and examination

Fig. 4 is changes of friction coefficient of respective solid lubricant films against temperature. They show (1) cases of solid lubricant films (specimens No. 1, 2, 3 and 4) whose compounding ratio of solid lubricant components was taken as constant at 50:50 (mass%) and mixing ratio of solid lubricant to binder was changed, and (2) cases of solid lubricant films (specimens No. 2, 5 and 6) whose mixing ratio of solid lubricant to binder was taken as constant at 20:80 (vol%) and compounding ratio of solid lubricant components was changed. The measuring results of abrasion loss after testing respective solid lubricant films are summarized and shown in Fig. 5. The abrasion loss is shown by average values of the wearing depth at the both ends and in the central part of abrasion \bar{h} .

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Fig. 4 High-temperature reciprocating friction wear test results



Temperature, °C

(a) specimen No. 1

solid lubricant : binder = 10:90 (vol%)

$\text{CaF}_2 + \text{BaF}_2$: Cr_2O_3 = 50:50 (mass%)

-o- raising temperature
-●- lowering temperature

Friction coefficient μ

Temperature, °C

(b) specimen No. 2

solid lubricant : binder = 20:80 (vol%)

$\text{CaF}_2 + \text{BaF}_2$: Cr_2O_3 = 50:50 (mass%)

-o- raising temperature
-●- lowering temperature

Friction coefficient μ

Temperature, °C

(c) specimen No. 3

solid lubricant : binder = 30:70 (vol%)

$\text{CaF}_2 + \text{BaF}_2$: Cr_2O_3 = 50:50 (mass%)

-o- raising temperature
-●- lowering temperature

Friction coefficient μ

Temperature, °C

(d) specimen No. 4

solid lubricant : binder = 40:60 (vol%)

$\text{CaF}_2 + \text{BaF}_2$: Cr_2O_3 = 50:50 (mass%)

-o- raising temperature
-●- lowering temperature

Friction coefficient μ

Temperature, °C

(e) specimen No. 5

solid lubricant : binder = 20:80 (vol%)

$\text{CaF}_2 + \text{BaF}_2$: Cr_2O_3 = 40:60 (mass%)

-○- raising temperature
 -●- lowering temperature

Friction coefficient μ

Temperature, °C

(f) specimen No. 6

solid lubricant : binder = 20:80 (vol%)

$\text{CaF}_2 + \text{BaF}_2$: Cr_2O_3 = 60:40 (mass%)

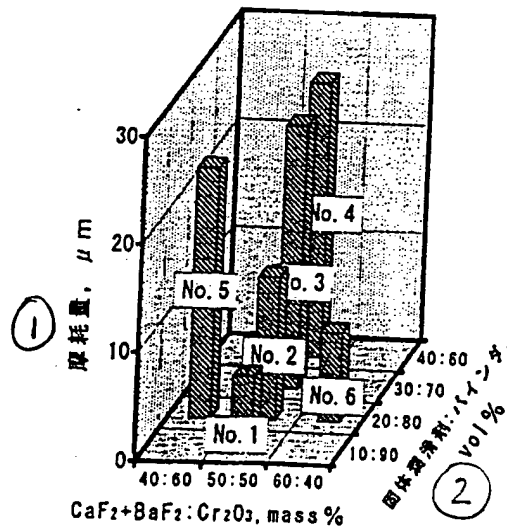


Fig. 5 Abrasion loss of solid lubricant films after high-temperature reciprocating friction wear tests

- (1) abrasion loss, μ
 (2) solid lubricant : binder, vol%

From Fig. 4, the friction coefficient decreased in the

temperature range of 700-800°C during raising temperature and in the temperature range of 800-400°C during lowering temperature with specimens No. 2, 3 and 4 of Fig. 4 (b), (c) and (d) of (1), but the friction coefficient did not decrease during raising or lowering temperature with specimen No. 1 of Fig. 4 (a). As a reason for it, it was considered that the solid lubricant necessary for the lubrication fully exists in the films of specimens No. 2, 3 and 4, but only a small quantity of solid lubricant was in the film of specimen No. 1.

With specimens No. 5 and No. 6 of Fig. 4 (e) and (f), the friction coefficient decreased only in the temperature range of 700-500°C during lowering temperature.

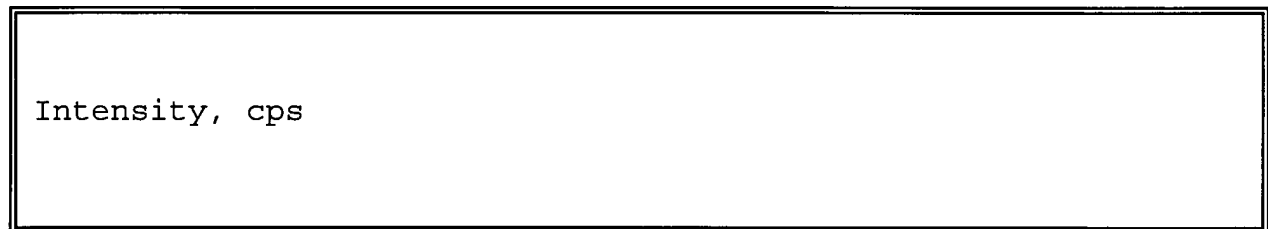
From the above results, it became clear that the solid lubricant existed in the films and the decrease of friction coefficient against temperature were found when the mixing ratio of solid lubricant was made to 20 vol% or above, and that the temperature range where the friction coefficient decreased was the widest when the compounding ratio of solid lubricant components was made to 50:50 (mass%).

From Fig. 5, it became clear that the abrasion loss of films increases with increasing the mixing ratio of solid lubricant in the solid lubricant films and increasing the compounding ratio of Cr_2O_3 in the solid lubricant components.

Next, in order to clarify the relationship between the temperature range where the friction coefficient decreased and the temperature at which a substance (BaCrO_4) considered to

contribute to the lubrication was formed in the films, the existence form of solid lubricant in the films against temperature was analyzed every 100°C from room temperature to 970°C by high-temperature X-ray diffraction with regard to the solid lubricant films which was formed simultaneously with specimen No. 2 and was not supplied to the high-temperature reciprocating friction wear tests. The analytic results above 700°C (970°C) are shown in Fig. 6.

Fig. 6 High-temperature X-ray diffraction results for confirming the formation of BaCrO₄ above 700°C



(a) diffraction pattern

agreement with BaCrO₄ peak

● - BaCrO₄ peak

(b) Check result of observed peak and BaCrO₄ peak

From the analytical results, it became clear that changes in the existence form of solid lubricant in the film were not specially found in the temperature range from room temperature to

600°C, but BaCrO₄ non-existent in the film up to that time was formed above 700°C. Thus, it became clear that a relationship between the test results of decrease in friction coefficient and the formation of BaCrO₄ exists in the temperature range from 700°C during raising temperature and up to 400°C during lowering temperature, and an excellent frictional property is exhibited by the coexistence of CaF₂ as described in the previous paper. Moreover, the reason why the friction coefficient increased was already described in the previous paper.

IV. SUMMARY

The frictional property, abrasion property and transfer property of solid lubricant formed by reduced pressure plasma spray method in its films were evaluated when the mixing ratio of solid lubricant to binder and the compounding ratio of solid lubricant components were changed, consequently the followings became clear.

(1) By the results of cage material evaluation tests, it was known that a solid lubricant film whose mixing ratio of solid lubricant to binder is 20:80 (vol%) and the compounding ratio of solid lubricant components is 50:50 (mass%) exhibits the most excellent frictional property, abrasion property and transfer property of as a solid lubricant for rolling ceramic bearing.

(2) By the results based on SEM observation and EPMA analysis, it became clear that a considerable quantity of solid lubri-

cant exists and uniformly distributes in the transfer film of roll-ing contact part of lower specimen in the case of solid lubricant film whose mixing ratio of solid lubricant to binder is 20:80 (vol%) and the compounding ratio of solid lubricant components is 50:50 (mass%).

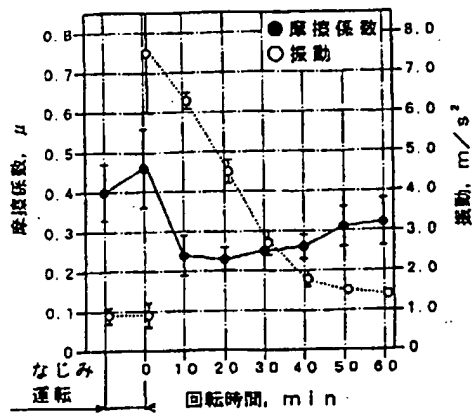
(3) By the results of high-temperature reciprocating friction wear tests, it was known that the friction coefficient decreases in /153
a wide temperature range in the solid lubricant films whose mixing ratio of solid lubricant to binder is 20 vol% or above and the friction coefficient shows the lowest stabilized value when the compounding ratio of solid lubricant components is made to 50:50 (mass%), and that the films become easy to wear with increasing the mixing ratio of solid lubricant in the solid lubricant films and the compounding ratio of Cr_2O_3 in the solid lubricant components.

(4) By the results of high-temperature X-ray diffraction, it became clear that BaCrO_4 is formed in the solid lubricant films at a temperature of above 700°C , a correlation between the decrease of friction coefficient in the solid lubricant films and the formation of BaCrO_4 in the films exists and an excellent frictional property is exhibited by the coexistence of CaF_2 .

References

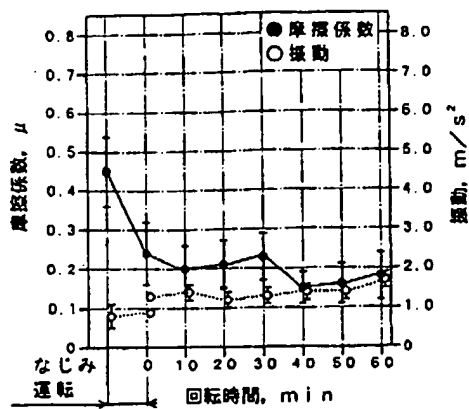
1. Shin Niizeki, Takeo Yoshioka, Hachiro Mizutani, Hiroshi

Toyota and Takanobu Hashimoto, *トライボロジスト (Tribologists)*, **40** (12),
1037 (1995) (Japanese).



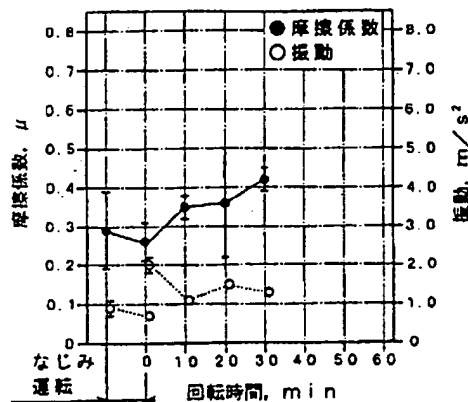
(a) 試験片 No. 1

固体潤滑剤：バインダ=10：90 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 50 : 50$ (mass %)



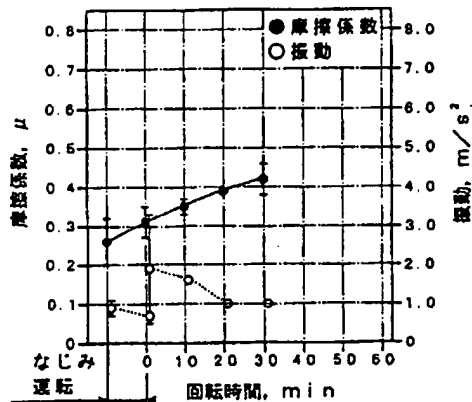
(b) 試験片 No. 2

固体潤滑剤：バインダ=20：80 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 50 : 50$ (mass %)



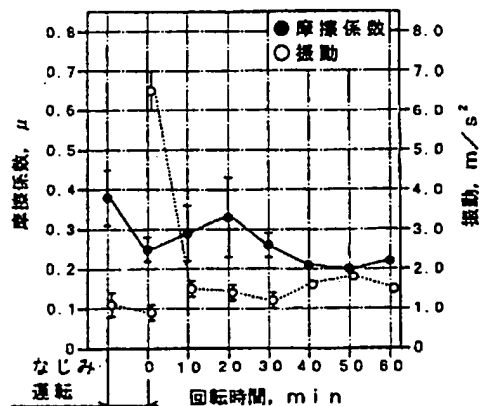
(c) 試験片 No. 3

固体潤滑剤：バインダ=30：70 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 50 : 50$ (mass %)



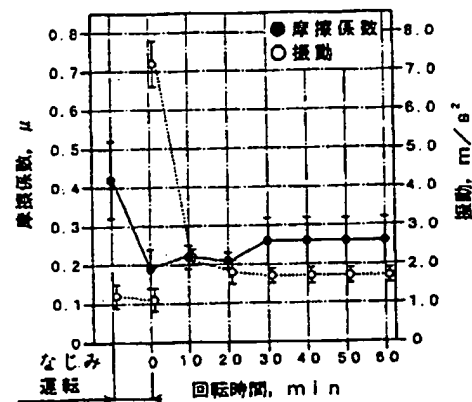
(d) 試験片 No. 4

固体潤滑剤：バインダ=40：60 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 50 : 50$ (mass %)



(e) 試験片 No. 5

固体潤滑剤：バインダ=20：80 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 40 : 60$ (mass %)



(f) 試験片 No. 6

固体潤滑剤：バインダ=20：80 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 60 : 40$ (mass %)

図1 保持器材料評価試験結果

み運転時に低
なり0.35程度
験開始後に高
程度の値で安

図1(d)の
み運転時から
0.42程度の高
始後に高くな
の値で安定し
については、摩
打ち切った。

以上から、
潤滑剤被膜が
らかとなった。

次に②につ
は、摩擦係数
ず、本試験開
度の値で安定
m/s²と高くな
の値で安定し

図1(f)の
み運転時に低
り0.25程度
に7.2 m/s²と
m/s²程度で安

以上から、
滑剤被膜が最
かとなった。

これらから、
合については、
た場合に摩擦
ること、固体
配合割合を50
係数および振
かとなった。

3.2 保持器材料

図2は、表
数および振動
被膜に対応し
量測定結果を
り接触部中央
試験片 No. 3

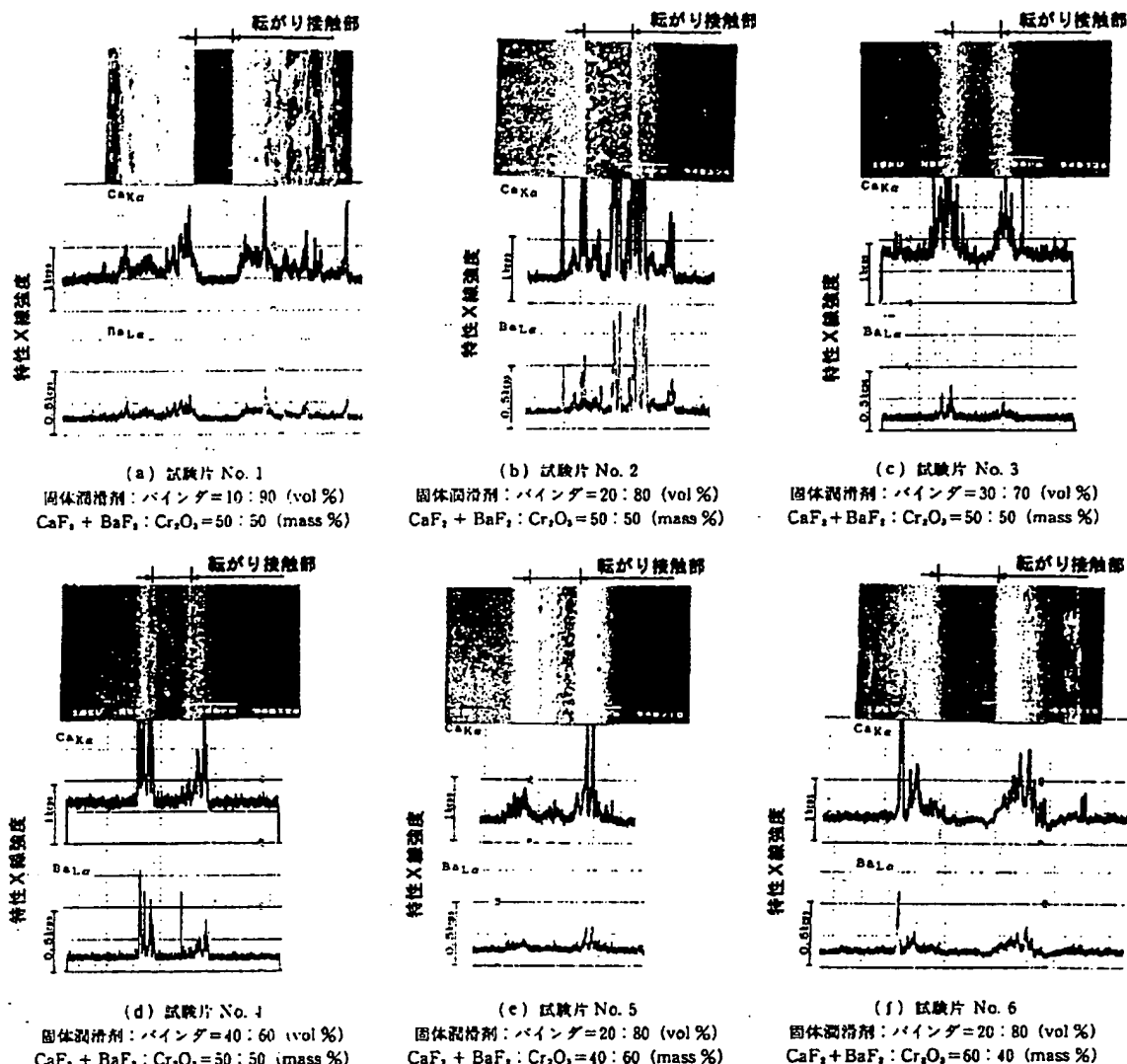


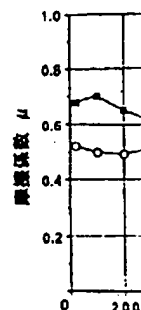
図3 SEM観察結果およびEPMAによる成分分析結果

部試験片の摩耗量が多くなったと考えられた。一方、固体潤滑剤成分の配合割合については、固体潤滑剤成分中のCr₂O₃の増加に従い被膜が移着しやすくなるため、Cr₂O₃の増加に対して下部試験片の転がり接触部における移着膜の残存が多くなり、移着膜の潤滑により摩耗量が減少したと考えられた。なお、すべての試験片に対応する上部試験片には移着膜が存在し摩耗は認められなかった。

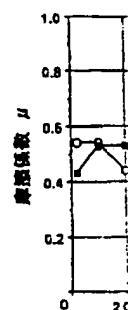
3.3 高温往復動摩擦摩耗試験結果と考察

図4は、それぞれの固体潤滑剤被膜の温度に対

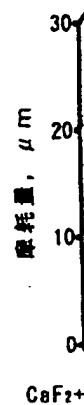
する摩擦係数の変化である。これらは、①固体潤滑剤成分の配合割合を50：50 (mass %) で一定とし、固体潤滑剤とバインダとの混合割合を変えた固体潤滑剤被膜（試験片 No. 1, 2, 3, 4）の場合と、②固体潤滑剤とバインダとの混合割合を20：80 (vol %) で一定とし、固体潤滑剤成分の配合割合を変えた固体潤滑剤被膜（試験片 No. 2, 5, 6）の場合とを示している。図5は、それぞれの固体潤滑剤被膜の試験後の摩耗量測定結果をまとめ示してある。摩耗量は摩耗こんの両端部と中央部の摩耗深さの平均値で示してある。



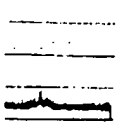
固体潤滑剤
CaF₂ + BaF₂



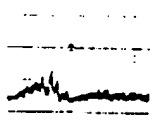
固体潤滑剤
CaF₂ + BaF₂

図5 高温
摩擦

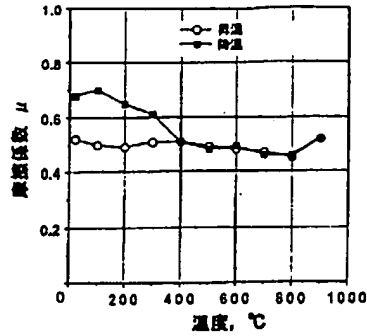
転がり接触部


No. 3
バインダ=30:70 (vol %)
CaF₂+BaF₂:Cr₂O₃=50:50 (mass %)

転がり接触部

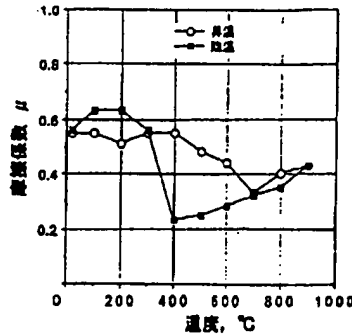

No. 6
バインダ=20:80 (vol %)
CaF₂+BaF₂:Cr₂O₃=40:60 (mass %)

①固体潤滑剤の混合割合を一定割合を変えて、3, 4)の混合割合を、潤滑剤成分の試験片 No. 2, 3, 4)それぞれ、それぞれ、試験結果を、両端部と中



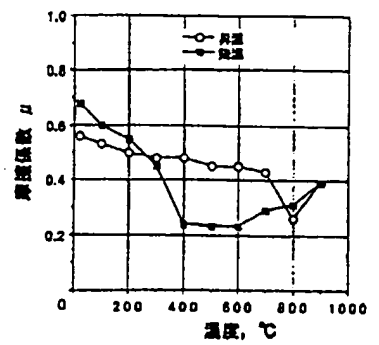
(a) 試験片 No. 1

固体潤滑剤：バインダ=10:90 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 50:50$ (mass %)



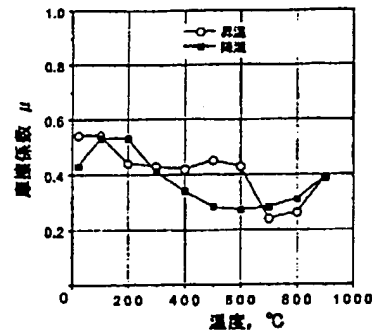
(b) 試験片 No. 2

固体潤滑剤：バインダ=20:80 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 50:50$ (mass %)



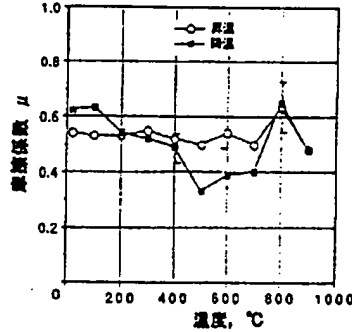
(c) 試験片 No. 3

固体潤滑剤：バインダ=30:70 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 50:50$ (mass %)



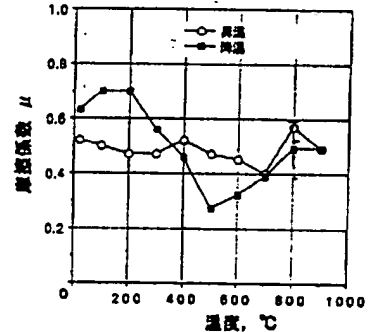
(d) 試験片 No. 4

固体潤滑剤：バインダ=40:60 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 50:50$ (mass %)



(e) 試験片 No. 5

固体潤滑剤：バインダ=20:80 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 40:60$ (mass %)



(f) 試験片 No. 6

固体潤滑剤：バインダ=20:80 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 60:40$ (mass %)

図4 高温往復動摩擦試験結果

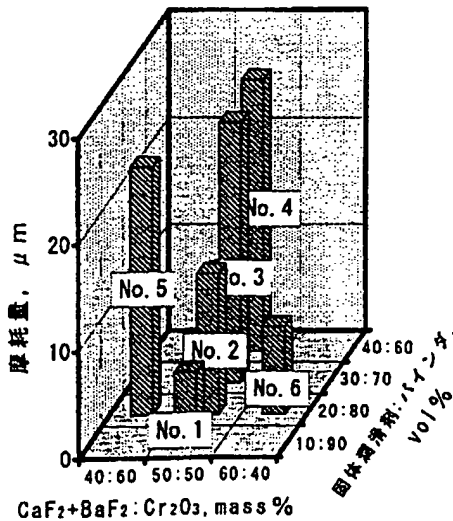


図5 高温往復動摩擦試験後の固体潤滑剤被膜の摩耗量

図4より、①については、図4(b), (c), (d)の試験片 No. 2, 3, 4で、昇温時の700 °Cから800 °C、および、降温時の800 °Cから400 °Cの温度範囲で摩擦係数が低下したが、図4(a)の試験片 No. 1では、昇温時および降温時とも摩擦係数は低下しなかった。この理由として、試験片 No. 2, 3, 4の被膜中には潤滑に必要な固体潤滑剤が十分存在したが、試験片 No. 1の被膜中には固体潤滑剤の量が少なかったと考えられた。

②については、図4(e), (f)の試験片 No. 5とNo. 6では、降温時の700 °Cから500 °Cの温度範囲でのみ摩擦係数が低下した。

以上の結果から、固体潤滑剤の混合割合を20 vol %以上にした場合、被膜中に固体潤滑剤が存在し、温度に対する摩擦係数の低下が認められること、また、固体潤滑剤成分の配合割合を50:

50 (mass %)にした場合、摩擦係数の低下する温度範囲が最も広いことが明らかとなった。

図5より、固体潤滑剤被膜中の固体潤滑剤の混合割合、また、固体潤滑剤成分中の Cr_2O_3 の配合割合が増加するに従い被膜の摩耗量が増加することが明らかとなった。

次に、摩擦係数の低下する温度範囲と、潤滑に寄与していると考えられる物質(BaCrO_4)が被膜中に形成される温度との関係を明らかにするため、試験片 No. 2 と同時に形成され、高温往復動摩擦摩耗試験に供されていない固体潤滑剤被膜について、温度に対する被膜中の固体潤滑剤の存在形態を高温X線回折により室温から970℃まで100℃ごとに分析した。図6には、700℃以上(970℃)での分析結果を示す。

分析の結果から、室温から600℃までの温度範囲では被膜中の固体潤滑剤の存在形態に特に変化は認められないが、700℃以上においてそれまで被膜中に存在しなかった BaCrO_4 が形成されることが明らかとなった。これより、昇温時の700℃から降温時の400℃までの温度範囲において摩擦係数が低下する試験結果と被膜中での BaCrO_4 の形成の間に相関性が存在し、前報で述べたように CaF_2 との共存により優れた摩擦特性を示すことが明らかとなった。なお、300℃以下

で摩擦係数が増加した理由については、すでに前報で述べた。

4. まとめ

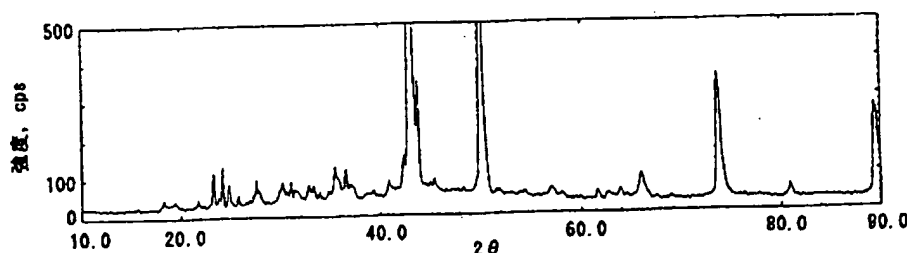
減圧プラズマ溶射法により形成した固体潤滑剤被膜において、固体潤滑剤とバインダとの混合割合および固体潤滑剤成分の配合割合を変えた場合について、その摩擦特性、摩耗特性ならびに移着特性を評価した結果、以下のことが明らかとなった。

(1) 保持材料評価試験の結果では、固体潤滑剤とバインダとの混合割合が20:80 (vol %), 固体潤滑剤成分の配合割合が50:50 (mass %)の固体潤滑剤被膜が、セラミック転がり軸受用固体潤滑剤として最も優れた摩擦特性、摩耗特性および移着特性を示すことがわかった。

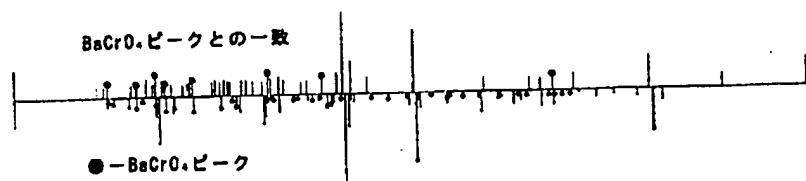
(2) 走査型電子顕微鏡による観察およびX線マイクロアナライザによる分析の結果、固体潤滑剤とバインダとの混合割合が20:80 (vol %), 固体潤滑剤成分の配合割合が50:50 (mass %)の固体潤滑剤被膜の場合に、下部試験片の転がり接触部の移着膜中に存在する固体潤滑剤量が多く、また、一様に分布していることが明らかとなった。

(3) 高温往復動摩擦摩耗試験の結果では、固体潤滑剤の混合割合が20 vol % 以上の固体潤滑剤

被膜において、低下し、また、50:50 (mass %)も低く安定した被膜中の固体潤滑剤成分中の(4)高温X線固体潤滑剤被膜



(a) 回折パターン



(b) 観察ピークと BaCrO_4 ピークとの照合結果

図6 700℃以上で BaCrO_4 の生成が確認された高温X線回折結果

論文

セラミック転がり軸受用
高温固体潤滑剤の開発 (第2報)—CaF₂+BaF₂とCr₂O₃からなる三元系固体潤滑剤—

原稿受付 1994年11月10日

"トライボロジスト" 第41巻 第2号 (1996) 146~153

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概 要 前報で、CaF₂+BaF₂+Cr₂O₃系固体潤滑剤の大気中高温雰囲気における潤滑特性について報告した。本報では、この固体潤滑剤について、固体潤滑剤とバインダとの混合割合および固体潤滑剤成分(CaF₂+BaF₂とCr₂O₃)の配合割合を変化させた場合の潤滑特性について評価を行った。その結果、この固体潤滑剤は、固体潤滑剤とバインダとの混合割合が20:80 (vol %) で、固体潤滑剤成分のCaF₂+BaF₂とCr₂O₃との配合割合が50:50 (mass %) の場合に、最も優れた潤滑性能を示すことが明らかとなった。また、高温X線回折の結果より、700℃から1000℃の温度範囲において固体潤滑剤被膜中にBaCrO₄が形成され、CaF₂との共存により優れた摩擦特性を示すことを前報に続いて確認した。

1. はじめに

前報¹⁾で、大気中500℃を超える高温雰囲気におけるセラミック転がり軸受の実用化を目標に、減圧プラズマ溶射法により形成した種々の固体潤滑剤被膜について、潤滑特性(摩擦特性、摩耗特性および移着特性)を評価・検討した結果を報告した。

著者らは、前報において優れた潤滑特性を示し

たCaF₂+BaF₂+Cr₂O₃系固体潤滑剤被膜について、固体潤滑剤とバインダとの混合割合および固体潤滑剤成分の配合割合を変化させて、さらに優れた固体潤滑剤の開発を試みた。

本論文では、試作した固体潤滑剤被膜について、転がり軸受の接触状態を模擬した保持器材料評価試験機により摩擦特性、摩耗特性および移着特性を評価した結果について述べる。さらに、高温往復動摩擦摩耗試験機により室温から900℃まで

Development of Solid Lubricants for High Temperature Rolling Ceramic Bearing (Part 2)

—Ternary System Solid Lubricants Composed of CaF₂ + BaF₂ and Cr₂O₃—

By Hiroshi TOYOTA, Research and Development Division, Koyo Seiko Co., Ltd. (24-1, Kokubuhiganyo-chō, Kashiwara-shi, Osaka 582), Takeo YOSHIOKA, Department of Advanced Machinery, Mechanical Engineering Laboratory (Namiki 1-2, Tsukuba-shi, Ibaraki 305), Kazunori UMEDA, Department of Material Science and Bioengineering, Mechanical Engineering Laboratory (ditto), Shin NIIZEKI, Research and Development Center, NSK Ltd. (5-50, Kugenuma-Shinmei 1-chōme, Fujisawa-shi, Kanagawa 251), Toshiaki KANEKO, Research and Development Bearing Engineering, NTN Corporation (3066, Oyumida, Higashikata, Kuwana-shi, Mie 511) and Takashi ITAKURA, Bearing Plant, NACHI-FUJIKOSHI Corp. (1-1, Fujikoshihonnachi 1-chōme, Toyama-shi, Toyama 930)

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PTO 98-0172

S.T.I.C. Translations Branch

の温度範囲においても報告する

2. 実験方法

2.1 固体潤滑

表1に試験にす。固体潤滑剤の3種類の粉末する試験片の径(インコネル®)を70L×17W>潤滑剤だけではとしてNi基合-0.5Y)粉末を固体潤滑剤移行なった。

2.2 保持器材

固体潤滑剤摩擦特性、摩耗保持器材料評価で評価した。

保持器材料

表1	
試験片 No.	固体潤滑剤配合、CaF ₂
1	
2	
3	
4	
5	
6	

バインダ: Ni-Zr

表2	
項目	
回転速度	(1)
設定温度	
荷重	
雰囲気	

の温度範囲における摩擦特性を評価した結果についても報告する。

2. 実験方法

2.1 固体潤滑剤被膜の形成方法

表1に試験に供した固体潤滑剤被膜の組成を示す。固体潤滑剤としては、 CaF_2 、 BaF_2 、 Cr_2O_3 の3種類の粉末を用いた。固体潤滑剤被膜を形成する試験片の母材は、前報と同様にNi-Cr合金（インコネル® 713 C）で製作し、試験片の形状を $70\text{L} \times 17\text{W} \times 14\text{H}$ (mm)とした。また、固体潤滑剤だけでは試験片に付着しないのでバインダとしてNi基合金（Ni-23.2 Co-17.0 Cr-12.5 Al-0.5 Y）粉末を用いた。

固体潤滑剤被膜の形成は、前報と同様の方法で行なった。

2.2 保持器材料評価試験と観察・分析

固体潤滑剤被膜を転がり軸受に適用した場合の摩擦特性、摩耗特性および移着特性を、前報の保持器材料評価試験機を用いて表2に示す試験条件で評価した。

保持器材料評価試験に供した固体潤滑剤被膜の

表1 固体潤滑剤被膜の組成

試験片 No.	固体潤滑剤成分の配合割合, mass % $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3$	固体潤滑剤とバインダとの混合割合, vol % 固体潤滑剤 : バインダ
1	50 : 50	10 : 90
2	50 : 50	20 : 80
3	50 : 50	30 : 70
4	50 : 50	40 : 60
5	40 : 60	20 : 80
6	60 : 40	20 : 80

バインダ：Ni-23.2 Co-17.0 Cr-12.5 Al-0.5 Y

表2 保持器材料評価試験条件

項目	内容
回転速度	1000 rpm (保持器材料試験片と転動体との滑り速度 = 2.2 m/s)
設定温度	800 °C 炉内雰囲気温度
荷重	保持器材料試験片-転動体：4.9 N 転動体-軌道輪：200 N
雰囲気	大気

摩擦特性、摩耗特性および移着特性の違いの原因を明らかにするため、保持器材料評価試験後の下部試験片の転がり接触部を、走査型電子顕微鏡（SEM）およびX線マイクロアナライザ（EPMA）により観察ならびに分析を行なった。

2.3 高温往復動摩擦摩耗試験と分析

固体潤滑剤被膜の広い温度範囲（室温～900 °C）における摩擦特性を、前報の高温往復動摩擦摩耗試験機を用いて評価した。

試験は、前報と同じ条件で行なった。摩擦係数の測定は、昇温時および降温時の各温度（100 °C間隔）で摩擦係数が安定した後に行なった。

広い温度範囲にわたって良好な潤滑特性を示した固体潤滑剤被膜について、その被膜中における固体潤滑剤の存在形態を高温X線回折（High Temperature X Ray Diffraction）により確認した。

3. 実験結果と考察

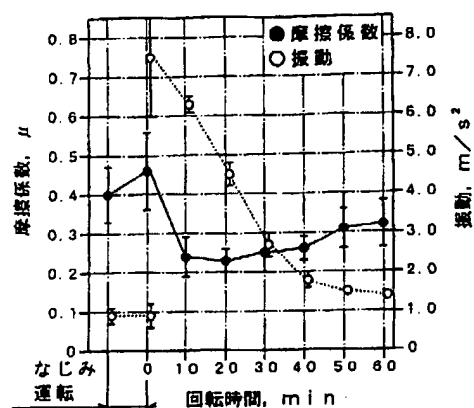
3.1 保持器材料評価試験結果

図1は、表1に示した固体潤滑剤被膜の摩擦係数および振動の経時変化である。これらは、①固体潤滑剤成分（ $\text{CaF}_2 + \text{BaF}_2$ 、 Cr_2O_3 ）の配合割合を50 : 50 (mass %) で一定とし、固体潤滑剤とバインダとの混合割合を変えた固体潤滑剤被膜（試験片 No. 1, 2, 3, 4）の場合と、②固体潤滑剤とバインダとの混合割合を20 : 80 (vol %) で一定とし、固体潤滑剤成分の配合割合を変えた固体潤滑剤被膜（試験片 No. 2, 5, 6）の場合とを示している。

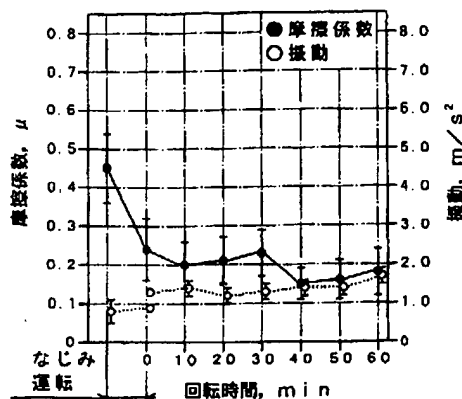
①については、図1(b)の試験片 No. 2 では、摩擦係数はなじみ運転時に低下し、本試験開始時点から0.2程度の値で経時的に安定していた。振動は本試験開始時点から1.5 m/s²程度の値で経時的に安定していた。

これに対し図1(a)の試験片 No. 1 では、摩擦係数はなじみ運転時には低下せず本試験開始後に低下し0.25程度の値となり、その後徐々に高くなる傾向を示した。振動は本試験開始直後7.5 m/s²と高くなったが、その後徐々に低下し1.5 m/s²程度の値で安定した。

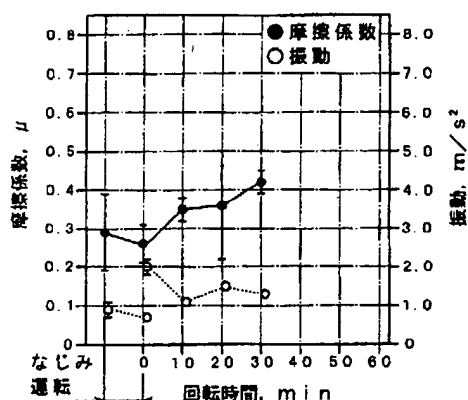
図1(c)の試験片 No. 3 では、摩擦係数はなじ



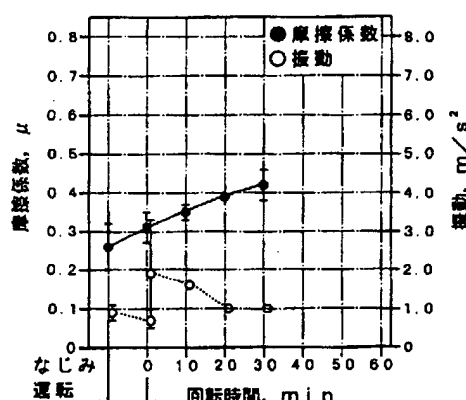
(a) 試験片 No. 1
 固体潤滑剤：バインダ=10：90 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 50 : 50$ (mass %)



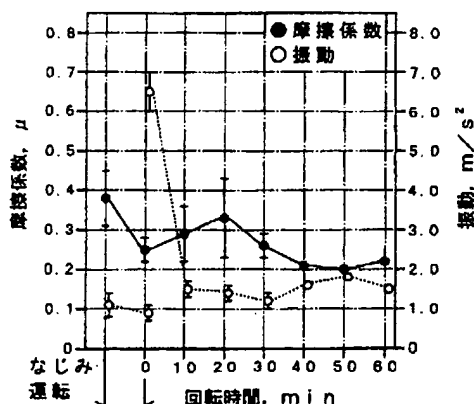
(b) 試験片 No. 2
 固体潤滑剤：バインダ=20：80 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 50 : 50$ (mass %)



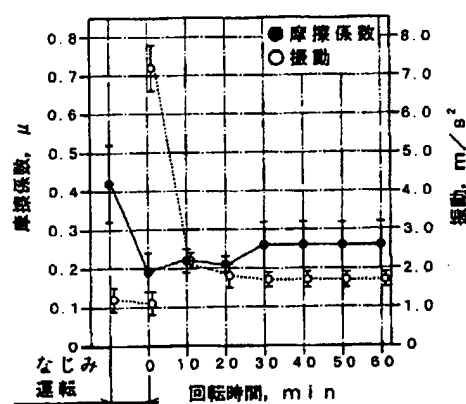
(c) 試験片 No. 3
 固体潤滑剤：バインダ=30：70 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 50 : 50$ (mass %)



(d) 試験片 No. 4
 固体潤滑剤：バインダ=40：60 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 50 : 50$ (mass %)



(e) 試験片 No. 5
 固体潤滑剤：バインダ=20：80 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 40 : 60$ (mass %)



(f) 試験片 No. 6
 固体潤滑剤：バインダ=20：80 (vol %)
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3 = 60 : 40$ (mass %)

図1 保持器材料評価試験結果

み運転時に低下
 なり 0.35 程度。
 試験開始後に高
 程度の値で安定

図1(d)の
 み運転時から約
 0.42 程度の高
 始後に高くな
 の値で安定した
 ついては、摩擦
 打ち切った。

以上から、①
 潤滑剤被膜が
 らかとなった。

次に②につい
 は、摩擦係数に
 ず、本試験開
 度の値で安定
 m/s^2 と高くな
 の値で安定し

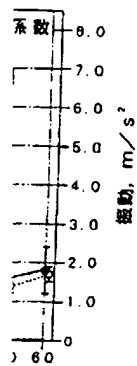
図1(f)の
 み運転時に低
 り 0.25 程度で
 に 7.2 m/s^2 と
 m/s^2 程度で安

以上から、②
 滑剤被膜が最
 かとなった。

これらから、
 合については、
 た場合に摩擦
 ること、固体
 配合割合を 50
 係数および振
 かとなった。

3.2 保持器材

図2は、表
 数および振動
 被膜に対応し
 量測定結果を
 り接触部中央
 試験片 No. 3



み運転時に低下したが、本試験開始後徐々に高くなり0.35程度の高い値で安定した。振動は本試験開始後に高くなったが、すぐに低下し1 m/s²程度の値で安定した。

図1(d)の試験片 No. 4 では、摩擦係数はなじみ運転時から徐々に高くなり続け、本試験開始後0.42程度の高い値で安定した。振動は本試験開始後に高くなったが、すぐに低下し1 m/s²程度の値で安定した。なお、試験片 No. 3 と No. 4 については、摩擦係数が0.4を超えた時点で試験を打ち切った。

以上から、①においては、試験片 No. 2 の固体潤滑剤被膜が最も優れた潤滑特性を示すことが明らかとなった。

次に②については、図1(e)の試験片 No. 5 では、摩擦係数はなじみ運転時に低下したが安定せず、本試験開始後再び高くなり最終的に0.2程度の値で安定した。振動は本試験開始後に6.5 m/s²と高くなったがすぐに低下し1.5 m/s²程度の値で安定した。

図1(f)の試験片 No. 6 では、摩擦係数はなじみ運転時に低下したが本試験開始後徐々に高くなり0.25程度で安定した。振動は本試験開始後に7.2 m/s²と高くなったが、すぐに低下し1.8 m/s²程度で安定した。

以上から、②においても試験片 No. 2 の固体潤滑剤被膜が最も優れた潤滑特性を示すことが明らかとなった。

これらから、固体潤滑剤とバインダとの混合割合については、混合割合を20:80 (vol %)にした場合に摩擦係数および振動とも低く安定していること、固体潤滑剤成分の配合割合については、配合割合を50:50 (mass %)にした場合に摩擦係数および振動とも低く安定していることが明らかとなった。

3.2 保持器材料評価試験結果の考察

図2は、表1に示した固体潤滑剤被膜の摩擦係数および振動の平均値と、それぞれの固体潤滑剤被膜に対応した下部試験片の転がり接触部の摩耗量測定結果をまとめて示している。摩耗量は転がり接触部中央部の摩耗深さである。なお、図2の試験片 No. 3 と No. 4 の摩耗量は試験時間30分

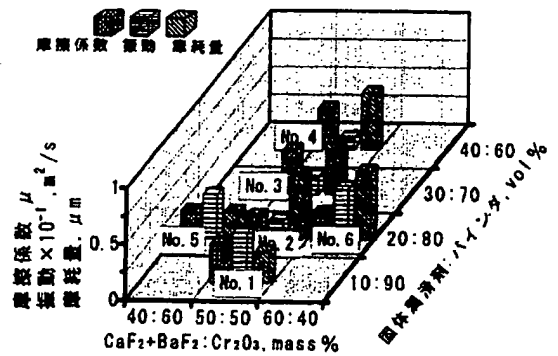


図2 保持器材料評価試験結果まとめ

間の値であり、他の試験片の摩耗量は試験時間60分間のものである。図3は、表1の固体潤滑剤被膜に対応した下部試験片の転がり接触部のSEM像とEPMAによる分析結果である。

図2より、固体潤滑剤被膜の摩擦係数および上部試験片と下部試験片との転がり接触部で発生する振動は、固体潤滑剤とバインダとの混合割合が20:80 (vol %), 固体潤滑剤成分の配合割合が50:50 (mass %) の場合に最も良好な結果を示すことがわかる。

この理由として、図3より、それぞれの固体潤滑剤被膜に対応した下部試験片中、固体潤滑剤とバインダとの混合割合が20:80 (vol %) の試験片 No. 2 と No. 5 に対応した下部試験片の転がり接触部に移着膜が認められること、ならびに固体潤滑剤成分の配合割合が50:50 (mass %) の試験片 No. 2 の移着膜中に固体潤滑剤が多く存在しかつ一様に分布していることが考えられた。

次に、図2と図3から摩耗量について考察する。試験片 No. 3 と No. 4 の試験時間が30分であったことを考慮すると、固体潤滑剤とバインダとの混合割合を変化させた場合では、固体潤滑剤の混合割合が増加するに従い摩耗量が増加する傾向が認められる。また、固体潤滑剤成分の配合割合を変化させた場合では、Cr₂O₃ の配合割合が増加するに従い摩耗量の減少および転がり接触部に移着膜が残存する傾向が認められる。

この理由として、被膜中の固体潤滑剤の混合割合が増加するに従い被膜が脆くなり摩耗しやすくなって、移着しても短時間で潤滑膜が消耗し、下

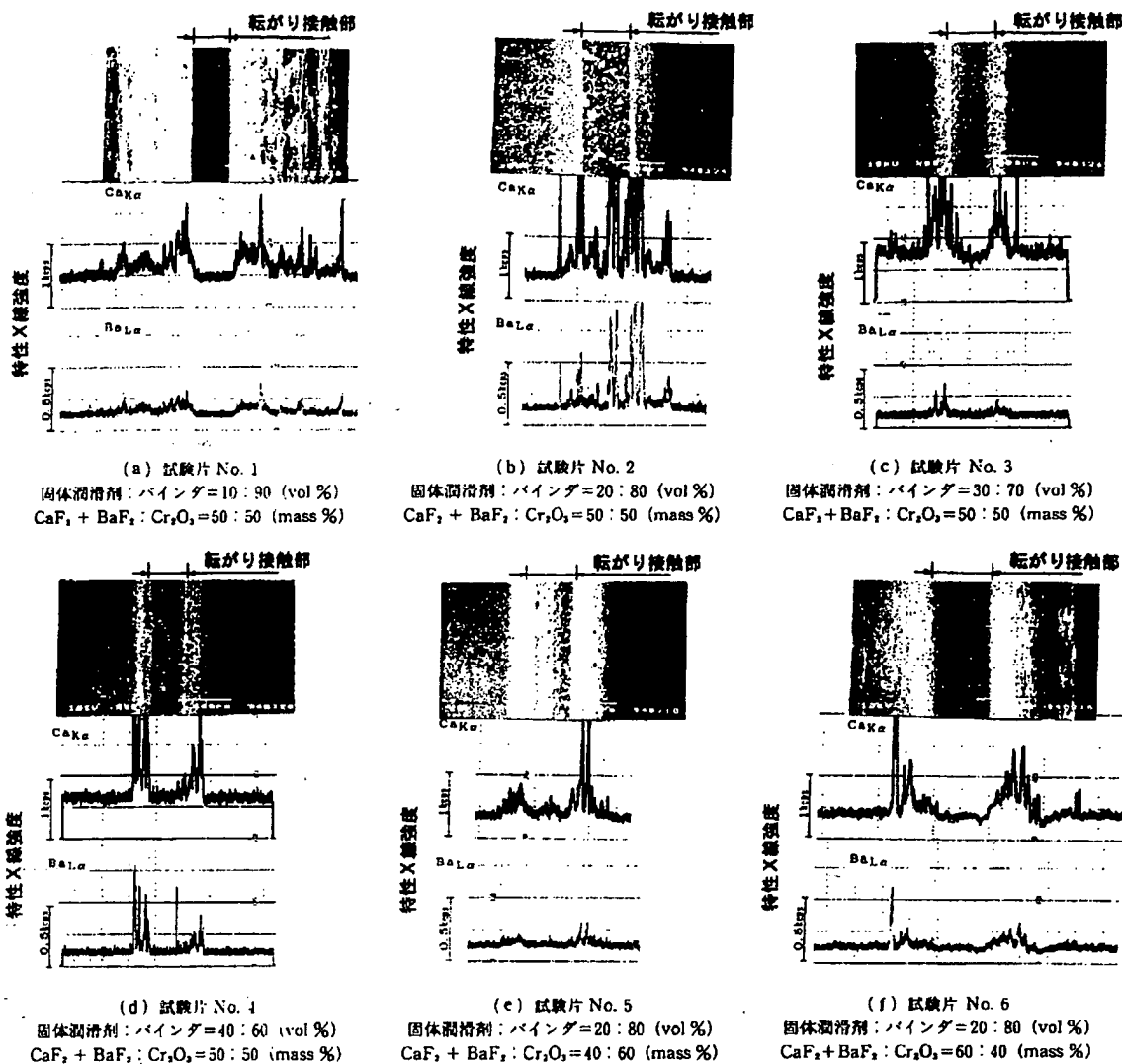


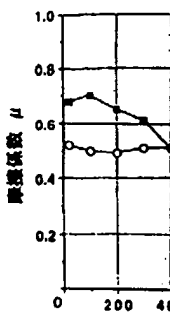
図3 SEM観察結果およびEPMAによる成分分析結果

部試験片の摩耗量が多くなったと考えられた。一方、固体潤滑剤成分の配合割合については、固体潤滑剤成分中の Cr_2O_3 の増加に従い被膜が移着しやすくなるため、 Cr_2O_3 の増加に対して下部試験片の転がり接触部における移着膜の残存が多くなり、移着膜の潤滑により摩耗量が減少したと考えられた。なお、すべての試験片に対応する上部試験片には移着膜が存在し摩耗は認められなかった。

3.3 高温往復動摩擦摩耗試験結果と考察

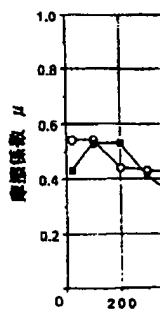
図4は、それぞれの固体潤滑剤被膜の温度に

する摩擦係数の変化である。これらは、①固体潤滑剤成分の配合割合を50 : 50 (mass %) で一定とし、固体潤滑剤とバインダとの混合割合を変えた固体潤滑剤被膜 (試験片 No. 1, 2, 3, 4) の場合と、②固体潤滑剤とバインダとの混合割合を20 : 80 (vol %) で一定とし、固体潤滑剤成分の配合割合を変えた固体潤滑剤被膜 (試験片 No. 2, 5, 6) の場合とを示している。図5は、それぞれの固体潤滑剤被膜の試験後の摩耗量測定結果をまとめ示してある。摩耗量は摩耗こんの両端部と中央部の摩耗深さの平均値で示してある。



(a)

固体潤滑剤 : バイ
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3$



(b)

固体潤滑剤 : バイ
 $\text{CaF}_2 + \text{BaF}_2 : \text{Cr}_2\text{O}_3$

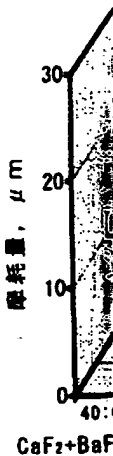


図5 高温往復動摩擦摩耗試験結果

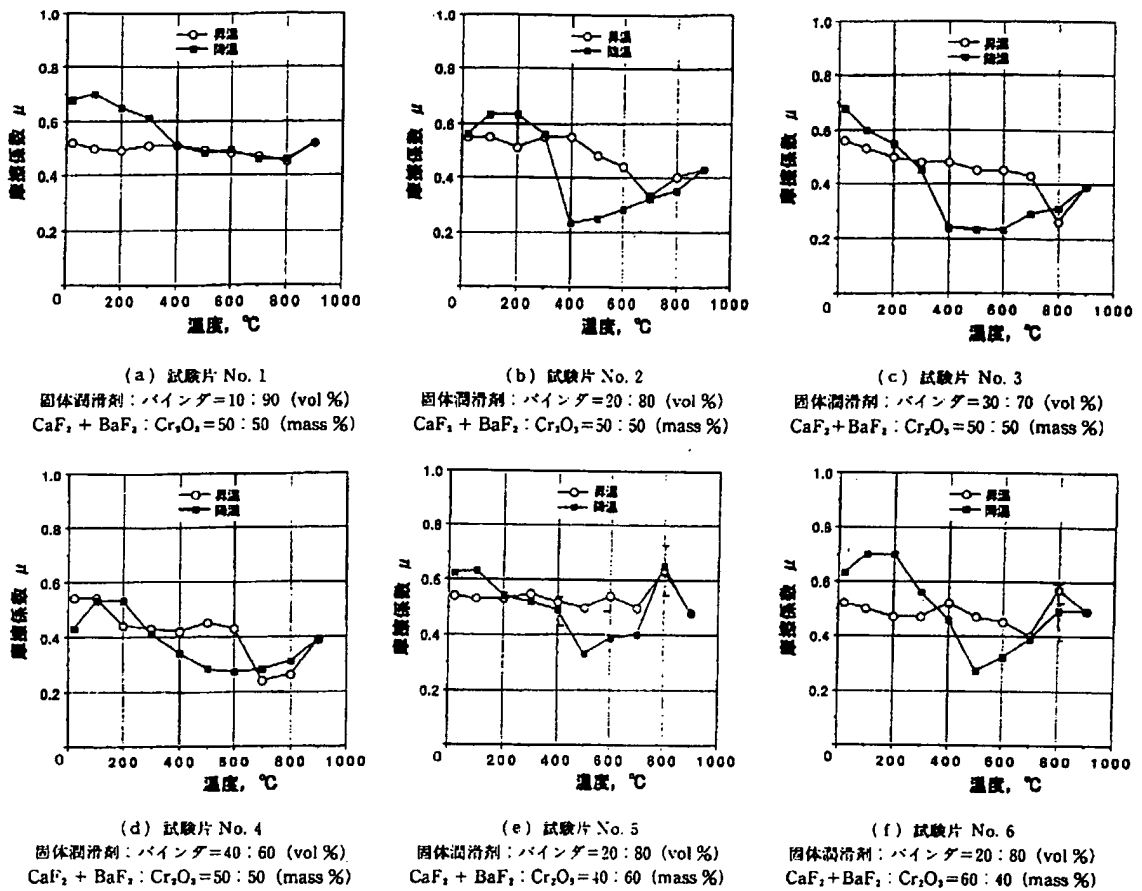
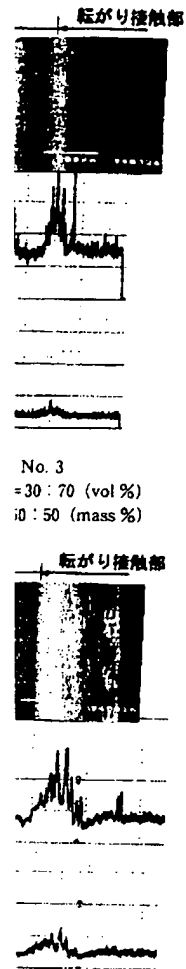


図4 高温往復動摩擦摩耗試験結果

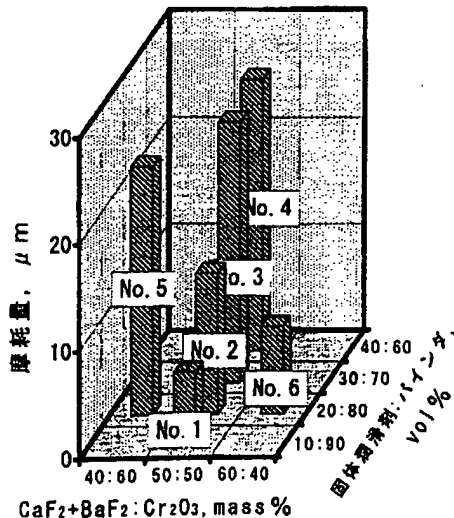


図5 高温往復動摩擦摩耗試験後の固体潤滑剤被膜の摩耗量

図4より、①については、図4(b)、(c)、(d)の試験片 No. 2, 3, 4で、昇温時の700℃から800℃、および、降温時の800℃から400℃の温度範囲で摩擦係数が低下したが、図4(a)の試験片 No. 1では、昇温時および降温時とも摩擦係数は低下しなかった。この理由として、試験片 No. 2, 3, 4の被膜中には潤滑に必要な固体潤滑剤が十分存在したが、試験片 No. 1の被膜中には固体潤滑剤の量が少なかったと考えられた。

②については、図4(e)、(f)の試験片 No. 5とNo. 6では、降温時の700℃から500℃の温度範囲でのみ摩擦係数が低下した。

以上の結果から、固体潤滑剤の混合割合を20 vol %以上にした場合、被膜中に固体潤滑剤が存在し、温度に対する摩擦係数の低下が認められること、また、固体潤滑剤成分の配合割合を50:

50 (mass %) にした場合、摩擦係数の低下する温度範囲が最も広いことが明らかとなった。

図5より、固体潤滑剤被膜中の固体潤滑剤の混合割合、また、固体潤滑剤成分中の Cr_2O_3 の配合割合が増加するに従い被膜の摩耗量が増加することが明らかとなった。

次に、摩擦係数の低下する温度範囲と、潤滑に寄与していると考えられる物質(BaCrO_4)が被膜中に形成される温度との関係を明らかにするため、試験片 No. 2 と同時に形成され、高温往復動摩擦摩耗試験に供されていない固体潤滑剤被膜について、温度に対する被膜中の固体潤滑剤の存在形態を高温X線回折により室温から970℃まで100℃ごとに分析した。図6には、700℃以上(970℃)での分析結果を示す。

分析の結果から、室温から600℃までの温度範囲では被膜中の固体潤滑剤の存在形態に特に変化は認められないが、700℃以上においてそれまで被膜中に存在しなかった BaCrO_4 が形成されることが明らかとなった。これより、昇温時の700℃から降温時の400℃までの温度範囲において摩擦係数が低下する試験結果と被膜中での BaCrO_4 の形成の間に相関性が存在し、前報で述べたように CaF_2 との共存により優れた摩擦特性を示すことが明らかとなった。なお、300℃以下

で摩擦係数が増加した理由については、すでに前報で述べた。

4. まとめ

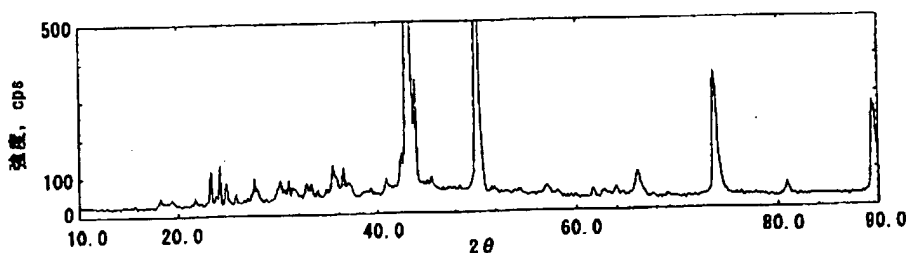
減圧プラズマ溶射法により形成した固体潤滑剤被膜において、固体潤滑剤とバインダとの混合割合および固体潤滑剤成分の配合割合を変えた場合について、その摩擦特性、摩耗特性ならびに移着特性を評価した結果、以下のことが明らかとなった。

(1) 保持材料評価試験の結果では、固体潤滑剤とバインダとの混合割合が20:80 (vol %), 固体潤滑剤成分の配合割合が50:50 (mass %) の固体潤滑剤被膜が、セラミック転がり軸受用固体潤滑剤として最も優れた摩擦特性、摩耗特性および移着特性を示すことがわかった。

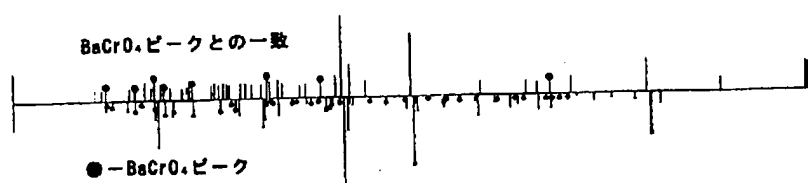
(2) 走査型電子顕微鏡による観察およびX線マイクロアナライザによる分析の結果、固体潤滑剤とバインダとの混合割合が20:80 (vol %), 固体潤滑剤成分の配合割合が50:50 (mass %) の固体潤滑剤被膜の場合に、下部試験片の転がり接触部の移着膜中に存在する固体潤滑剤量が多く、また、一様に分布していることが明らかとなった。

(3) 高温往復動摩擦摩耗試験の結果では、固体潤滑剤の混合割合が20 vol % 以上の固体潤滑剤

被膜において、低下し、また、50:50 (mass %) も低く安定した被膜中の固体潤滑剤成分中の() 被膜が摩耗し (4) 高温X線固体潤滑剤被膜



(a) 回折パターン



(b) 観察ピークと BaCrO_4 ピークとの照合結果

図6 700℃以上で BaCrO_4 の生成が確認された高温X線回折結果

は、すでに前

た固体潤滑剤
グとの混合割合
を変えた場合
ならびに移着
明らかとなっ

固体潤滑剤
(vol %), 固
(mass %) の
り軸受用固体
摩耗特性およ

およびX線マ
固体潤滑剤
(vol %), 固
(mass %) の
の転がり接
剥離が多く、
らかとなった。
果では、固体
り固体潤滑剤

被膜において、摩擦係数が広い温度範囲において低下し、また、固体潤滑剤成分の配合割合を50:50 (mass %) にした場合に、摩擦係数は最も低く安定した値を示すこと、また、固体潤滑剤被膜中の固体潤滑剤の混合割合、および、固体潤滑剤成分中の Cr_2O_3 の配合割合が増加するに従い被膜が摩耗しやすくなることがわかった。

(4) 高温X線回折の結果、700℃以上の温度で、固体潤滑剤被膜中に BaCrO_4 が形成されること、

ならびに摩擦係数が低下することと被膜中での BaCrO_4 の形成の間に相関性が存在し、 CaF_2 との共存により優れた摩擦特性を示すことが明らかとなった。

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